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Laboratory and Field Evaluation of the Semi-Vost (Semi-Volatile Organic Sampling Train) Method

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LABORATORY AND FIELD
EVALUATION OF THE
SEMI-VOST METHOD

by

J. Bursey, J. Steger, M. Palazzolo,
D. Benson, J. Homolya, R. McAllister,
J. McGaughey, and D. Wagoner
Radian Corporation
3200 E. Chapel Hill Road/Nelson Highway
Research Triangle Park, North Carolina 27709

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Project Officer

John Margeson
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27709

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

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Laboratory studies and a second field evaluation have been completed to assess the performance of the Semi-Volatile Organic Sampling Train (Semi-VOST) method for measuring concentrations of principal organic hazardous constituents (PDHCs) with boiling points greater than 100°C emitted from hazardous waste incineration. The Semi-VOST methodology was tested initially through a series of laboratory experiments and a field test at a hazardous waste incinerator. In the first field test method precision and bias were shown to be compound specific. Laboratory studies demonstrated that method precision and bias were related to the distribution and recovery of POHCs throughout the components of the sampling train. Distribution and recovery of a POHC are related to boiling point, water solubility, and chemical functionality.

Additional laboratory experiments have demonstrated that, since basic organic compounds form salts by reaction with the acidic and wet environment found in stack emissions sampled with the Semi-VOST method, these compounds can be recovered by appropriate treatment of aqueous train components. Water soluble compounds were recovered from the aqueous portions of the Semi-VOST train. Based on these findings, a screening procedure was developed to select the extraction solvent and to estimate the analytical recovery of the test compounds from acidic water condensate using the Semi-VOST sample preparation methodology.

The second field test was performed at a hazardous waste incinerator using five gaseous deuterated compounds to dynamically spike four simultaneously operating Semi-VOST trains, Toluene, 1,1,2,2-tetrachloroethane, and chlorobenzene were chosen because of boiling point and chemical functionality. Pyridine was selected based on its potential to form a salt in the presence of hydrochloric acid. o-Xylene was added because of its large predicted retention volume on XAD-2® resin and its use as an internal standard in laboratory experiments. Estimates of method precision and bias are given for d_5-pyridine, d_8-toluene, d_5-chlorobenzene, d_{10}-o-xylene, and d_2-1,1,2,2-tetrachloroethane. Results of distributive volume experiments to verify chromatographically determined retention volumes are presented for each test compound.

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Laboratory studies and a second field evaluation have been completed to assess the performance of the Semi-Volatile Organic Sampling Train (Semi-VOST) method for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C emitted from hazardous waste incineration. The Semi-VOST methodology was tested initially through a series of laboratory experiments and a field test at a hazardous waste incinerator. In the first field test method precision and bias were shown to be compound specific. Laboratory studies demonstrated that method precision and bias were related to the distribution and recovery of POHCs throughout the components of the sampling train. Distribution and recovery of a POHC are related to boiling point, water solubility, and chemical functionality.

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VOLUME I

SECTION 1
INTRODUCTION

The Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1975 (RCRA), requires that the Environmental Protection Agency establish a national regulatory program to ensure that hazardous wastes are managed in a manner which does not endanger human health or the environment. The statute requires EPA to promulgate performance standards for hazardous waste management. Included in the regulations that have been promulgated are provisions for waste disposal by incineration and requirements that hazardous waste incinerators be so operated that the principal organic hazardous constituents (POHCs) are destroyed and/or removed with a minimum efficiency of 99.99 percent. To determine destruction and removal efficiency (DRE), EPA has designated the Semi-Volatile Organic Sampling Train (Semi-VOST) Method as the method for measuring flue gas concentrations of POHCs with boiling points greater than 100°C.

The Quality Assurance Division of the EPA Environmental Monitoring Systems Laboratory (EMSL) has responsibility for evaluating and standardizing EPA source test methods. Under contract to EMSL, Radian Corporation is providing technical assistance in evaluating the Semi-VOST Method. The objective of the Semi-VOST program is to provide the data necessary to determine the bias, precision, applicability, and limitations of the method.

The technical approach used to collect these data is a multi-task effort involving literature, laboratory, and field studies. Literature and laboratory studies were conducted and an initial field test was performed.[1] The field test, which utilized a quad-train approach, provided preliminary data on method bias and precision. As a result of the recommendations developed from the first field study,[1] additional laboratory studies of the sample preparation steps and a second field test at a hazardous waste incinerator were performed.

The experimental design of the laboratory evaluations and the second Semi-VOST test was based on experience gained from the initial test and data gathered from previous laboratory studies.[1] The second test again utilized a quad-train to evaluate the method performance by sampling flue gas from a full-scale incinerator while spiking test compounds into the sample trains. The objectives of the program were to:

- design and conduct an experimental laboratory program to evaluate compound stability in the extraction solvent and the effect of water solubility and compound functionality on the recovery of selected test compounds;

- develop a screening procedure for Appendix VIII water-soluble compounds to provide information for selecting an extraction solvent and for estimating recovery of water-soluble compounds from the acidic water condensate;

- design, construct, and evaluate the performance of a dynamic spiking system using deuterated test compounds;

- carry out a second field test at a hazardous waste incineration facility to provide additional data on method precision and bias for additional test compounds; and

- compare retention volumes determined in the laboratory for selected test compounds on XAD-2® resin with values determined in the field by a series of distributive volume experiments sampling flue gas from a hazardous waste incinerator.

Conclusions and recommendations from the laboratory and field study are presented in Sections 2 and 3, respectively. The Semi-VOST method is presented in detail in Appendix A and is summarized in Section 4.

The laboratory study conducted to determine compound stability and evaluate the sample preparation steps under controlled conditions is discussed in Section 5. The results of this laboratory evaluation were incorporated into the most recent version of the Semi-VOST method. The final stage of the evaluation required a second field test. The results of the second field test are summarized in Section 6 of this report.

SECTION 2
CONCLUSIONS AND FINDINGS

Several major conclusions can be drawn from the Semi-VOST laboratory and field studies conducted to date.

- From the first field study, method precision and bias were shown to be compound specific and could not be generalized for all classes of organic compounds. Laboratory and field experiments demonstrated that method precision and bias are related to the distribution and recovery of a particular POHC throughout the components of the sampling train.

- Sample distribution and recovery of POHCs are related to boiling point, water solubility, and chemical functionality. The second field study verified these conclusions through experiments using a variety of POHCs exhibiting a range of boiling points, water solubilities, and chemical functionalities.

- XAD-2® adsorbent samples must be extracted immediately after removal from the resin cartridge for optimum analyte recoveries. Samples that are allowed to stand in Soxhlets at room temperature prior to extraction may lose compounds. The compound loss due to volatilization is related to its vapor pressure.

- Dynamic spiking of the Semi-VOST train using deuterated compounds was demonstrated as a viable approach to determine method bias under field conditions. In the absence of measurable stack emissions of POHCs, dynamic spiking can be used to measure method precision.

- Method precision for d_5-pyridine was 17.7 percent coefficient of variation. This value was derived from 16 determinations of percent recovery from field test data using the dynamic spiking system. Method bias calculated from these data was -29.0 percent.

- Method precision for d_8-toluene was 14.6 percent coefficient of variation and method bias was -14.9 percent, derived from 13 determinations of percent recovery during the second field test. These values compare favorably with a method bias of +1.0 percent determined for toluene in the first field study.[1]

- Method precision for d_{10}-*o*-xylene was 8.1 percent coefficient of variation and method bias was -0.9 percent, derived from 13 determinations of percent recovery for the same field test.

- Method precision for d_2-tetrachloroethane was 32.9 percent coefficient of variation and method bias was -18.5 percent, derived from 13 determinations of percent recovery for the same field test. An estimate of method bias from the first field study was -16.0 percent.

- Method precision for d_5-chlorobenzene was 13.7 percent coefficient of variation and method bias was -13.8 percent, derived from 13 determinations of percent recovery for the same field test. In the first field study, method precision for chlorobenzene was estimated to be 19.9 percent. Method bias for chlorobenzene was not determined in the first field study because of the large concentration of chlorobenzene in the stack gas.

- All compounds spiked on XAD-2® resin with the exception of d_2-tetrachloroethane exhibited better precision and recovery than pyridine, which was collected in the condensate and impingers. The poorer precision for d_2-tetrachloroethane is in part due to the variability in the measurement of this compound near the method detection limit.

- The field test distributive volume experiments demonstrated that d_{10}-*o*-xylene and d_2-tetrachloroethane did not break through the XAD-2® resin bed and that the retention volume determined experimentally in the laboratory was not exceeded. Therefore, the Semi-VOST method is adequate for the sampling and analysis of d_{10}-*o*-xylene and d_2-tetrachloroethane.

- The field test distributive volume experiments for d_8-toluene and d_5-chlorobenzene confirmed that, for sample volumes greater than the retention volumes determined in the laboratory, the total compound mass collected on the resin departs from a linear correlation with the sample volume. This result verifies that laboratory data can be used to predict field retention volumes for POHCs.

- Retention volumes determined chromatographically in the laboratory were used to determine sampling volumes for the field test. Experimental data from the field test support the use of laboratory-determined retention volumes to predict field breakthrough volumes.

- Pyridine is a basic organic compound which reacts with aqueous hydrochloric acid to form an organic chloride salt, which is highly water soluble. Approximately 88 percent of the pyridine is collected in the back-half (impinger solutions) of the Semi-VOST train.

- A difference in holding time before extraction for dynamically spiked XAD-2® samples (35 days *vs*. 63 days) does not result in a significant difference in recoveries for all of the compounds spiked.

- If the volume of condensate requires multiple extractions and concentrations, the extract of the aqueous train components should be combined with the XAD-2® extract at the final concentration step.

- A comparison was made between observed values and expected levels of five compounds spiked onto XAD-2® as quality control samples provided by the Research Triangle Institute. The percent bias ranged from -1.84 percent to -8.90 percent with reference to the RTI values. Average percent bias was -4.68 percent. The agreement is excellent, showing that the recovery of organic compounds from XAD-2® resin using the Semi-VOST methodology is favorable.

- The use of surrogate standards during sample preparation and analysis is necessary to obtain the best representation of test compound recoveries. Deuterated analogs, when available, are the best possible surrogates because they behave exactly the same as the compounds of interest and will be truly representative of test compound recoveries.

SECTION 3
RECOMMENDATIONS

Based on the results of the method evaluation studies presented in this report, recommendations for future work follow.

- A literature review should be conducted to categorize Appendix VIII[2] compounds according to water solubility, chemical similarity and adsorption strength (retention volume) on XAD-2® to allow estimates of method precision and bias for compound classes, since method bias and precision have been shown to be compound specific. Predicted values should be verified by experiment.

- Laboratory studies have demonstrated that low compound recoveries can be attributed to either poor chromatographic properties, selection of inappropriate solvent for extraction, or compound reaction with the aqueous components of the sampling train which become acidic during sample collection. Further laboratory studies are warranted to extend these observations and to use Semi-VOST screening procedures to determine the applicability of the sample preparation and analysis steps to other Appendix VIII[2] compounds or classes of compounds.

- Earlier laboratory studies demonstrated low compound recoveries associated with NO_x flue gas levels.[1] Variation in compound recovery with NO_x level should be studied using solutions of nitric acid to simulate condensate and impinger contents for evaluating compound reactivity with NO_x. The results of the laboratory studies could then be used to plan an additional field evaluation of the method to include artifact formation.

- Laboratory and field studies should be performed to differentiate between resin artifacts and Products of Incomplete Combustion (PICs) present in XAD-2® resin resulting from sampling of stack emissions from hazardous waste combustion.

- Particulate filters from selected Semi-VOST trains should be challenged with known POHC concentrations to evaluate POHC-particulate matter interactions during sample collection.

- Further laboratory and field evaluation studies should include an evaluation of the applicability of the Semi-VOST method to the measurement of Appendix VIII aldehydes, aromatic amines such as diphenylamine, and compounds that can only be analyzed by high performance liquid chromatography (HPLC) with a selective detector.

SECTION 4
METHOD FORMULATION

In the application of the Semi-VOST method described in "Sampling and Analysis Procedures for the Determination of Semi-Volatile Compounds from Combustion Sources" (submitted as Appendix A, "Laboratory and Field Evaluation of the Semi-VOST Method," Volume II, PB86 123569112, September 5, 1985), gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. Key elements of the train (as shown in Figure 1) include a high-efficiency particulate filter and a packed bed of a porous polymeric adsorbent resin (XAD-2®). The filter is used to separate stack gas particles from gaseous substances which are then adsorbed onto XAD-2®. As a collection sorbent, XAD-2®, a polystyrene-divinylbenzene copolymer, has the advantage of high surface area (300 m^2/g) with an average pore size of 9 nm (90 Å) for collection of semi-volatile compounds. Following sample collection, the train components are extracted with solvent, the extracts concentrated, and specific compounds are identified/quantified using high resolution gas chromatography coupled with low resolution mass spectrometry. If the proposed POHCs are water-soluble, these compounds can be evaluated prior to the field study using the Semi-VOST screening procedure to: 1) select the best extraction solvent; and 2) estimate recovery from the acidic water condensate.

After return of the samples to the laboratory, all fractions are spiked with surrogate standards prior to extraction, concentration, and analysis. The use of surrogates provides a measure of the efficiency of the sample preparation procedures. In the sample analyses, an examination of surrogate recovery is used to qualify and possibly adjust the analytical results. For example, poor or variable surrogate

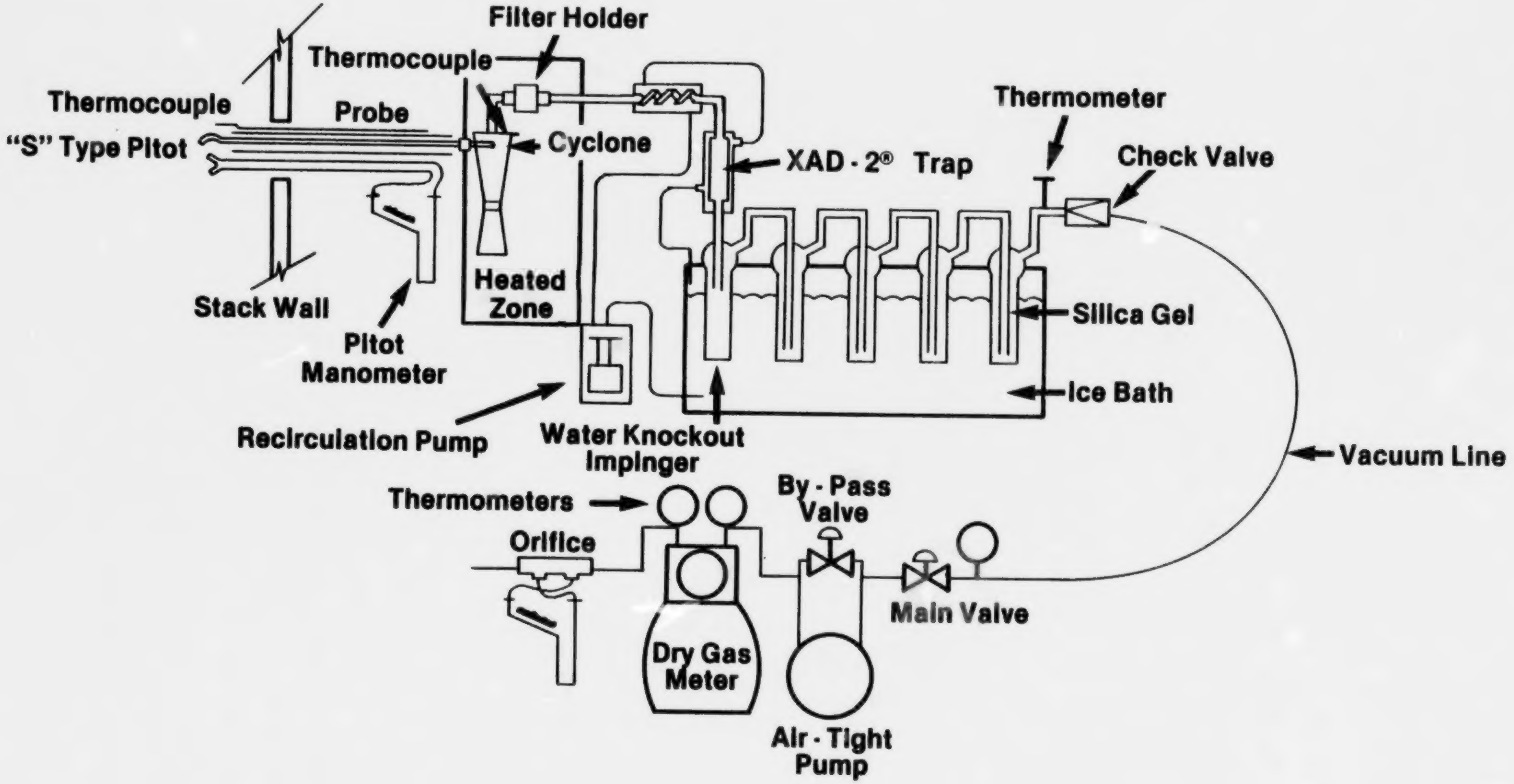

Filter Holder
Thermocouple
Thermocouple
Probe
"S" Type Pitot
Cyclone
XAD - 2® Trap
Thermometer
Check Valve
Stack Wall
Heated Zone
Silica Gel
Pitot Manometer
Ice Bath
Recirculation Pump
Water Knockout Impinger
Vacuum Line
Thermometers
By - Pass Valve
Orifice
Main Valve
Dry Gas Meter
Air - Tight Pump

Figure 1. Semi - VOST Sampling Train

recovery suggests difficulties with sample preparation/analysis rather than difficulties with incinerator operation. The surrogate compounds should be stable isotopically-labeled analogs of the compounds of interest or compounds that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis. Potential surrogate spiking compounds include: deuterated ethylbenzene, naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and ^{13}carbon-labeled pentachlorophenol.

The XAD-2® resin is spiked with surrogate standards and transferred with the filter to an all-glass Soxhlet extraction thimble. The module is rinsed with methylene chloride, the solution is added to the Soxhlet, and extraction is conducted for 16 hours. After extraction the solution is transferred from the Soxhlet extractor to a separatory funnel to allow phase separation. The water phase from the separatory funnel is combined with the water knockout impinger solution prior to acid/base methylene chloride extraction. The methylene chloride is removed from the separatory funnel and dried with sodium sulfate as it is added to the Kuderna-Danish (K-D) concentrator. Samples are concentrated to less than 10 mL, and a final volume adjustment made.

The water knockout impinger solution is spiked with surrogates, transferred to a separatory funnel, acidified, and extracted with methylene chloride. The aqueous phase is made alkaline and re-extracted with methylene chloride. The methylene chloride solutions are dried (passed through sodium sulfate) and subsequently combined in a K-D evaporator/concentrator and reduced in volume usually to less than 10 mL prior to adding a quantitation standard for GC/MS.

Impinger contents are extracted with methylene chloride under both acidic and basic conditions and then concentrated to a final volume. The methylene chloride/methanol rinses of the probe and filter housing are prepared by spiking with surrogate standards and adding sufficient water to a separatory funnel to force methylene chloride to become immiscible with water/methanol, forming two distinct phases. The water/methanol phase is extracted with methylene chloride under both acidic and basic conditions, dried, then concentrated. The water/methanol extract is combined with the XAD-2® resin extract prior to final K-D concentration.

Analysis is performed by GC/MS using a fused silica capillary GC column. The mass spectrometer is operated in a full scan (35 to 450 daltons) mode. Electron ionization (EI) spectra are collected since a majority of the potential POHCs produce reasonable EI spectra, which are compatible with the NBS Library of Mass Spectra and other reference data which aid in identification.

For quantitation by GC/MS, each sample fraction is spiked with a known amount of quantitation standard prior to analysis. The response ratio of the appropriate quantitation standard to each compound of interest in the sample is then compared to a similar ratio established with a calibration curve.

The Semi-VOST method (Appendix A) was followed for the second field study with the following exceptions:

- There were four co-located sampling trains at this site. The trains were operated simultaneously sampling stack gas from the same point with a quad probe.

- Rinses of Semi-VOST train components collected during sample recovery were: (1) a rinse with methanol; and (2) a second rinse with an equal portion of methylene chloride. These rinses were combined according to the analytical protocol.

- The water phase resulting from a separatory funnel separation of the methylene chloride extract of the XAD-2® resin was combined with the condensate knockout trap solution prior to an acid/base methylene chloride extraction.

- To accommodate the high moisture content of the effluent, an oversized knockout impinger along with a backup was added to the trains during the retention volume studies.

SECTION 5

LABORATORY EVALUATION

Previous evaluation[1] of the Semi-VOST method has shown that method precision and bias are compound specific. Laboratory experiments demonstrated that method precision and bias are related to the distribution and recovery of a particular POHC throughout the components of the sampling train. Sample distribution and recovery of a POHC are related to boiling point, water solubility, and chemical functionality.

With these parameters in mind several laboratory experiments were performed prior to the second field test.

- Define XAD-2® adsorbent resin interactions and/or analytical procedure interferences responsible for poor and/or variable recoveries of particular POHCs.

- Evaluate method interferences due to interaction with or in the solvent matrix by determining the stability of aniline, pyridine, phenol, and resorcinol in the extraction solvent (methylene chloride).

- Develop a method for screening Appendix VIII POHCs to identify interactions with Semi-VOST analytical procedures.

- Determine the retention volumes of toluene, 1,1,2,2-tetrachloroethane, chlorobenzene, pyridine, and o-xylene on XAD-2® resin to estimate breakthrough volumes for field distributive volume experiments.

Results and recommendations based on the laboratory experiments are presented below:

- To assess any interferences due to solvent interactions, the stabilities of aniline, pyridine, phenol, and resorcinol in methylene chloride were evaluated. The concentrations of the four test compounds remained within 10 percent of the original value for up to 118 days. Therefore, no major solvent-compound interactions were observed during the typical Semi-VOST sample storage time.

- Aniline and pyridine, which are basic organic compounds, will react in an acidic environment to form salts. These salts are insoluble in methylene chloride but are soluble in water, which is also present in the system. These reactions to form salts and the Soxhlet extraction procedure are partially responsible for poor and variable recoveries from XAD-2® resin. Acid/base extraction must be performed on the aqueous phase from the XAD-2® resin to obtain good recovery of salt-forming compounds.

- Resorcinol is extremely water soluble, 123 g/100 g of water at 25°C, and will associate with any water present in the Semi-VOST train. This water, which may contain salts and/or water soluble compounds, is leached out of the XAD-2® resin during Soxhlet extraction by methylene chloride. When the methylene chloride layer is dried using sodium sulfate, all moisture is removed with the last of any salts or water soluble compounds, and poor recoveries result. The procedure used for analysis of the XAD-2® resin must be revised to include the extraction and analysis of any residual water extracted from the resin. An additional resin extraction using methanol is also recommended to retrieve any salts or water soluble compounds which may have been left in residual water on the resin. Compounds dissolved in this residual water are not extracted by methylene chloride. The methanol extraction is not necessary if, during method validation, methylene chloride has been demonstrated to extract the POHCs from the XAD-2® resin efficiently.

- Compounds of high water solubility such as resorcinol require extraction of the aqueous Semi-VOST train components with diethyl ether or tert-butyl ether rather than methylene chloride to improve the recovery.

- The extraction of XAD-2® adsorbent resin samples must begin immediately after removal from the resin cartridge. Volatilization of compounds with high vapor pressures will take place from samples that are allowed to remain in Soxhlets prior to extraction.

- The Semi-VOST screening procedure (details contained in the interim report, "Laboratory Evaluation of the Sample Preparation Semi-VOST Methodology for Measuring Semi-Volatile Organic Emissions From Hazardous Waste Incinerators," October 6, 1986) for water soluble compounds provides information for: 1) selecting an extraction solvent; and 2) estimating the recovery of water-soluble compounds from the acidic water condensate.

Toluene, 1,1,2,2-tetrachloroethane, and chlorobenzene were included in the first field test. Pyridine was selected based on its potential to form salts in the presence of hydrochloric acid. o-Xylene was added due to its large retention volume on XAD-2® resin and its use as an internal standard in the Semi-VOST laboratory experiments.

A definition of breakthrough or specific retention volume (V_g^T) is the sample volume required to elute a compound (adsorbate) which is introduced onto a XAD-2® resin (adsorbent) bed. Before breakthrough occurs, the amount of spiked material adsorbed on the bed is directly proportional to the volume sampled. Moreover, the adsorbate-sample volume relationship must pass through the origin. After the breakthrough volume has been reached, the amount of adsorbate is no longer proportional to sample volume, but approaches a horizontal asymptotic value equal to the equilibrium loading.

When using solid adsorbents for trapping and concentrating organic materials, it is desirable to have some means to estimate the efficiency of the procedure, especially to determine the maximum volume of gas that may be sampled before significant breakthrough occurs. To do this, investigators have made use of the physicochemical theory of gas chromatography. By treating packed adsorber tubes as a chromatographic column, investigators have measured retention volumes at various temperatures and used this information to extrapolate to the temperature at which the absorber tube is to be employed. The retention volume determination consists of packing a chromatographic column with the adsorbent and measuring the retention time of the analyte at various temperatures. The gas holdup time of a non-adsorbed material is subtracted and the result is multiplied by the carrier gas flow rate to yield the retention volume. Since the adsorbent will have a relatively large capacity at ambient temperatures, the measurements must be made at temperatures that are considerably higher in order to obtain resolvable chromatographic peaks. However the results are then extrapolated to an ambient temperature, e.g., to 20°C, and reported as retention volume per unit mass of adsorbent. This procedure has been widely employed in many laboratories,[3,4,5] and has been carried out in the present study for comparison with results obtained in actual field testing.

In practice, chromatographic measurements are made at several temperatures and values of ln (V/T) vs. 1/T are fitted by linear regression to obtain an equation from which the breakthrough volume estimates are made. (Some investigators[4] actually plot ln (V) vs. 1/T and accordingly obtain a regression slope that is not independent of temperature and that results in error if extrapolation is made over large temperature differences[6,7]). In the present study, retention volume estimates were made using the same lot of XAD-2® resin employed in the field test. Also, the carrier flow rate was selected to simulate the face velocity at the adsorbent cartridge. The results are listed in Table 1 for five compounds.

TABLE 1. RETENTION VOLUME

Compound	Retention Volume mL/g at $20^{\circ}C$	Sampling Flow Rate cfm[1]	Breakthrough Volume m^3 (ft^3)	Time for Breakthrough h
Toluene	137,277	0.50	2.72 (96)	3.2
1,1,2,2-Tetra-chloroethane	1,430,672	0.50	28.6 (1011)	33.7
Chlorobenzene	450,473	0.50	9.00 (318)	10.6
Pyridine	68,896	0.50	1.36 (48)	1.6
o-Xylene	1,021,676	0.50	20.4 (720)	24.0

[1] 0.50 cubic foot/minute (cfm) is equivalent to 0.000236 m^3/s.

Example calculation for toluene with 20 grams of adsorbent.

$$\text{Sampling time} = 137{,}277\ \frac{\text{mL}}{\text{gram}} \times \frac{1\ \text{liter}}{1000\ \text{mL}} \times 20\ \text{grams} \times \frac{1\ \text{ft}^3}{28.3\ \text{liters}} \times \frac{1\ \text{min}}{0.5\ \text{ft}^3} \times \frac{1\ \text{h}}{60\ \text{min}}$$

$$= 3.2\ \text{h}$$

SECTION 6

FIELD EVALUATION

The second Semi-VOST field evaluation was designed based on experience and data gained from the initial field and laboratory studies. Both the first and second field tests utilized a Semi-VOST train in a quad train configuration to evaluate method performance by sampling flue gas from a full-scale incinerator while spiking test compounds into the sample trains. The objectives of the second field test were to: 1) provide additional data on method bias and precision, 2) compare laboratory retention volume data for selected compounds to field data, and 3) evaluate the stability of selected compounds spiked onto the XAD-2® resin by both dynamic gaseous spiking and liquid spiking.

6.1 PROCESS DESCRIPTION AND TEST EQUIPMENT

6.1.1 Site Description

The second Semi-VOST field evaluation was conducted at a facility owned and operated by Smith-Kline Chemicals. An aqueous brine waste stream and spent solvents from the production of fine pharmaceuticals are destroyed at the site in a continuously operated hazardous waste incinerator.

The incinerator, shown schematically in Figure 2, is a down-fired liquid injection design manufactured by John Zink Company. The incinerator is operated at 12.7 to 15.8 MJ/h (12 to 15 million Btu/h) with a burner temperature of 1815°C (3300°F) and a gas temperature of 1010°C (1850°F). Natural gas is burned continuously to support combustion of the aqueous and solvent wastes. A caustic (NaOH) venturi scrubber, operated at a pressure drop of 17.4 to 19.9 kPa (70 to 80 inches of water), is used to control HCl emissions. The scrubber exit gas temperature is approximately 88°C (190°C).

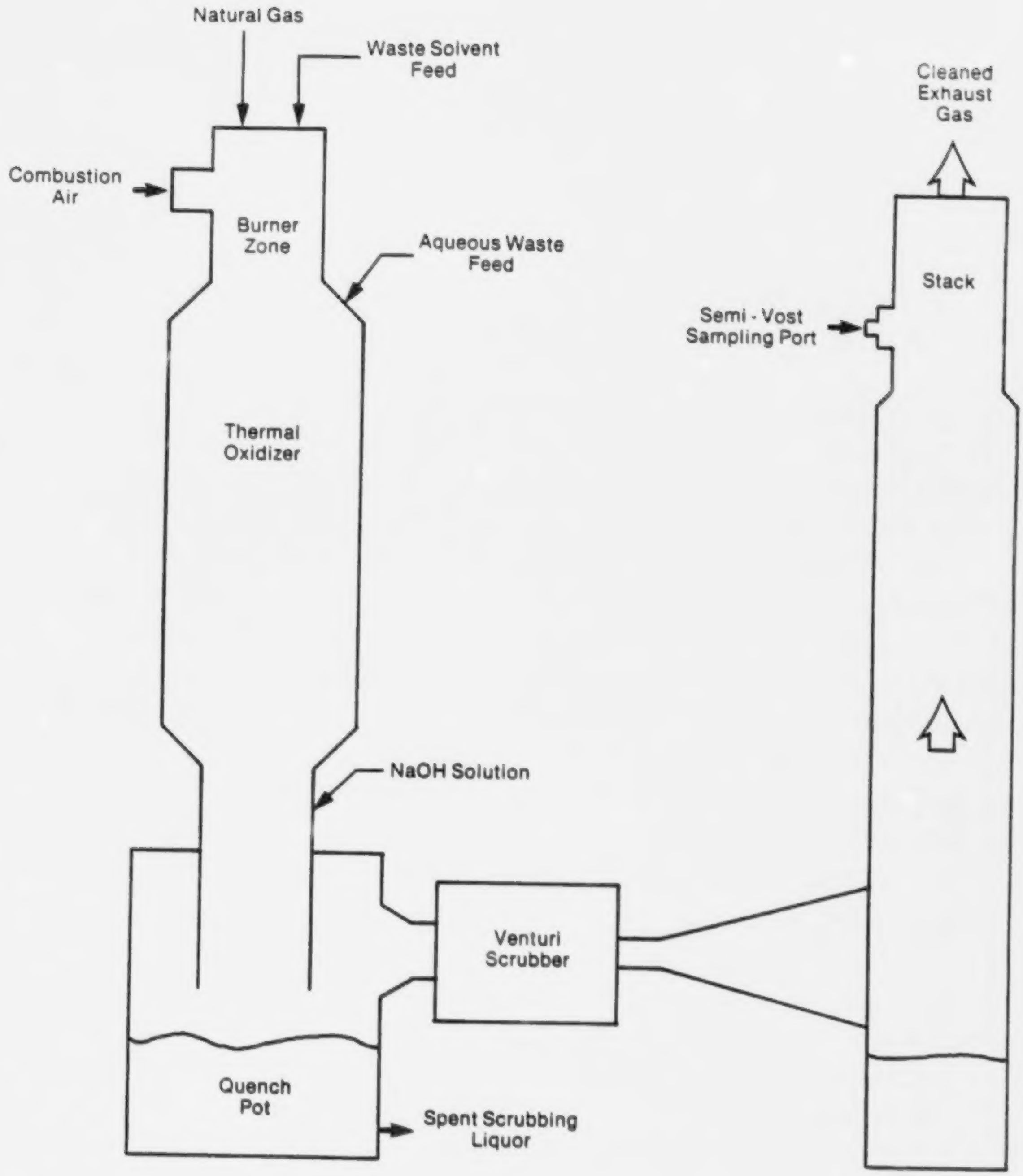

Natural Gas
Waste Solvent Feed
Cleaned Exhaust Gas
Combustion Air
Burner Zone
Aqueous Waste Feed
Stack
Semi - Vost Sampling Port
Thermal Oxidizer
NaOH Solution
Venturi Scrubber
Quench Pot
Spent Scrubbing Liquor

Figure 2. Diagram of Smith - Kline Incinerator

Waste solvent is fed to the incinerator from an agitated 90.9-m^3 (20,000-gallon) storage tank. In an attempt to provide precision estimates for the Semi-VOST method, the waste solvent feed was spiked with chlorobenzene and tetrachloroethylene at a level (approximately 4%) expected to provide detectable quantities of the compounds at the stack outlet.

6.1.2 Test Equipment

6.1.2.1 Quad-Probe

All of the samples were collected with a quad-probe sampling system connected to four identical sampling trains (see Figure 3). Regardless of changes in the stack gas composition over the sampling period, the four samples taken with each set of trains were virtually identical in composition. The set of four samples provided the basis for estimating the overall method precision, including sampling, sample preparation, and analysis.

6.1.2.2 Dynamic Spiking System

The dynamic spiking of the sampling trains with gas phase d_8-toluene, d_5-chlorobenzene, d_2-1,1,2,2-tetrachloroethane, d_5-pyridine, and d_{10}-o-xylene was accomplished utilizing the apparatus shown in Figure 4. The use of deuterated compounds is an effective technique to differentiate spiked test compounds from components of stack gas since it is unlikely that the incineration would be burning deuterated wastes. Specific components of the dynamic spiking system included separate pressure regulators and precision flow controllers for each sample train, a heat lamp, circulating fan, and a temperature controller to maintain constant temperature in the control box. A multichannel flow controller readout for monitoring the flow controllers was also included.

Two identical spiking systems were used - one for Trains A and B and one for Trains C and D. Each spiking system was fed by a low-pressure compressed gas cylinder containing a mixture of the five deuterated spiking compounds in high purity nitrogen, at a sample concentration equivalent to 100 times the minimum detection limit of the GC/MS system. The cylinders used for spiking were analyzed in the laboratory by GC/FID before and after the field test. Two of the

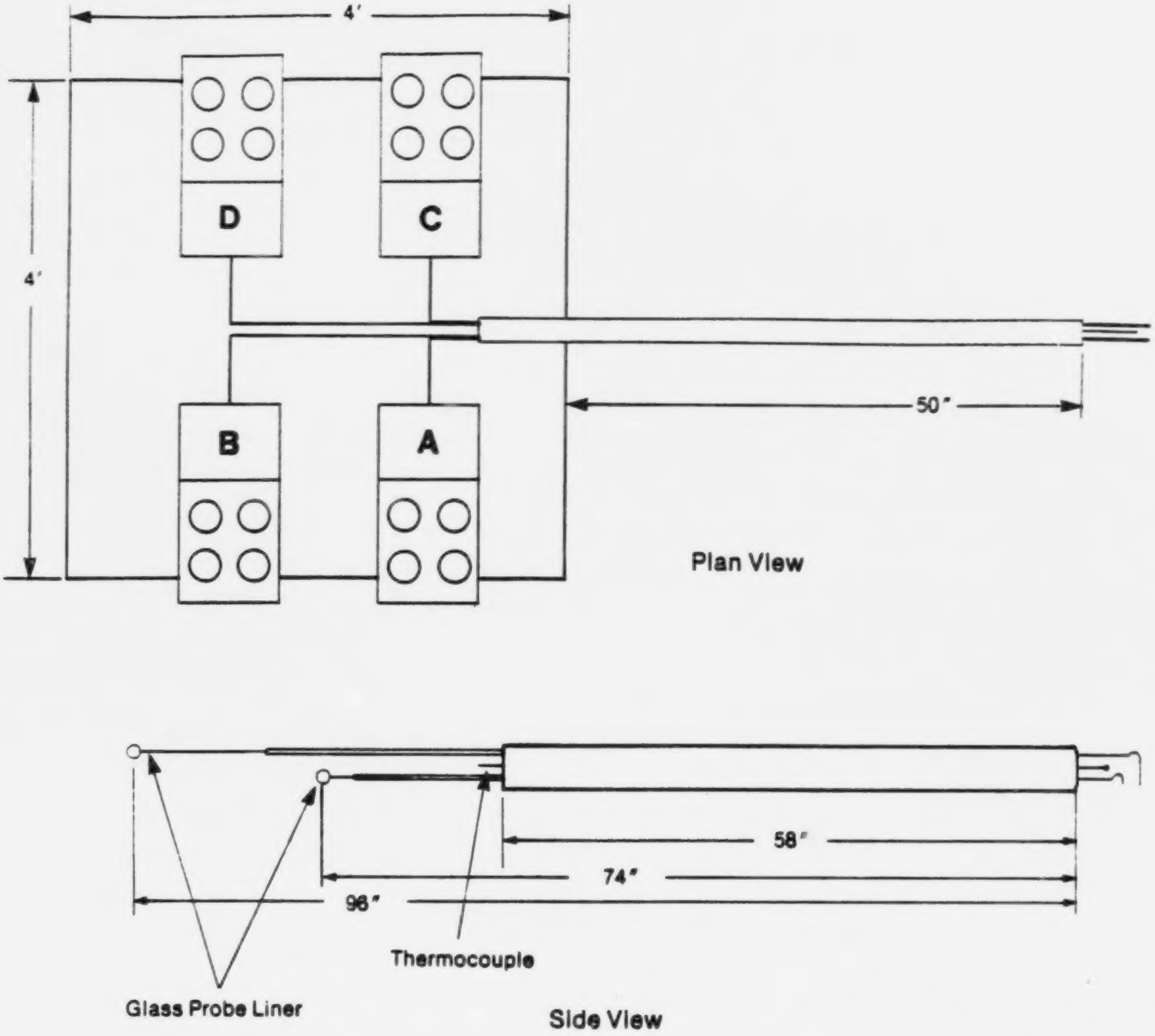
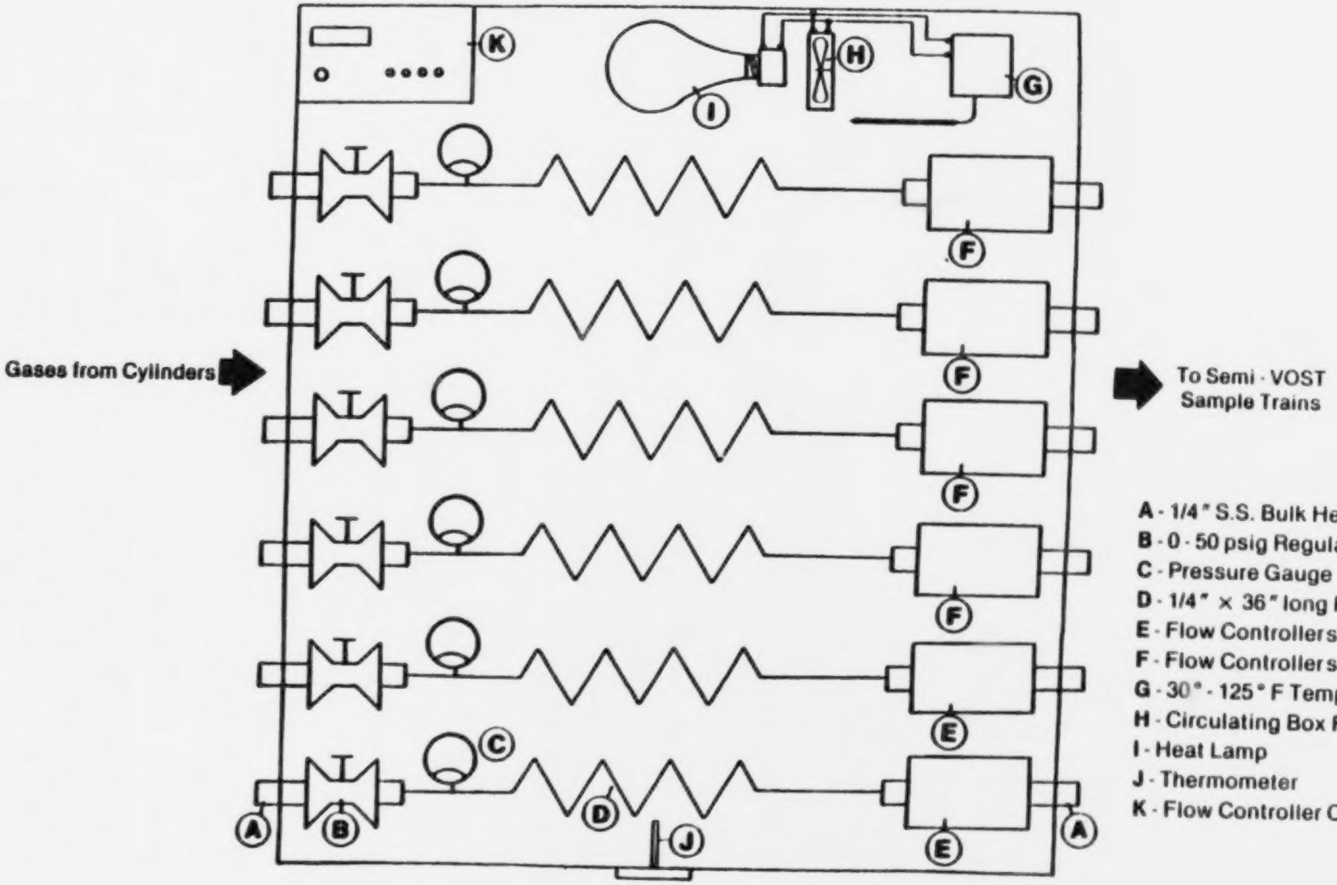

4'
4'
D
C
B
A
50"
Plan View
58"
74"
96"
Thermocouple
Glass Probe Liner
Side View

Figure 3. Quad - Train Configuration


Gases from Cylinders
To Semi - VOST Sample Trains
A
B
C
D
E
F
G
H
I
J
K

A - 1/4" S.S. Bulk Head Union
B - 0 - 50 psig Regulator
C - Pressure Gauge
D - 1/4" × 36" long Preheater Coil
E - Flow Controllers (0 - 10 slpm)
F - Flow Controllers (0 - 50 sccm)
G - 30° - 125° F Temperature Controller
H - Circulating Box Fan
I - Heat Lamp
J - Thermometer
K - Flow Controller Common Readout

Figure 4. Spiking System

cylinders were analyzed by GC/MS and were found to contain no detectable amounts of native compounds. All cylinders used in this program were prepared from the same deuterated stock.

The flow controllers on the dynamic spiking system were set to deliver 20 mL/min each to Trains A, B, C, and D. The gaseous spike entered each train through a glass "T" located after the filter and before the condenser of each train to eliminate any effects of interaction between particulate material trapped on the filter and the sample gas. Particulate filter effects will be studied in future experiments.

Teflon® lines [0.635-cm (1/4-inch) O.D.] connected the gas cylinders to the flow controllers. The flow controllers were housed in a thermostatically controlled environment maintained at approximately 32°C (90°F). Teflon® lines [0.3175-cm (1/8-inch) O.D.] sheathed in 0.635-cm Teflon® and foam insulation connected the flow controllers to the Semi-VOST sampling trains. A three-way valve was placed before the sampling train so that flow from the dynamic spiking system could be directed either to the sampling train or to exhaust. For proper operation, each flow controller required a minimum pressure drop of 137.9 kPa (20 psig). The pressure exiting the gas cylinders was maintained at 275.8 kPa (40 psig).

The spiking system described above was calibrated and tested in the laboratory prior to this field testing. The flow controllers were calibrated under operating conditions. Flow deliveries were also measured against a vacuum and were found not to be affected from 16.0 to 59.9 kPa (4.75 to 17.75 inches of Hg). The results of the preliminary laboratory tests showed that the spiking system required a minimal equilibration time of approximately two hours for accurate compound delivery.

6.1.2.3 Total Hydrocarbon Analysis

For each sampling period, the stack gas was monitored with a total hydrocarbon (THC) continuous monitor to provide data on the variability of the THC concentration of the stack gas during the sampling period and from one run to the next. Analysis for total hydrocarbons (THC) was performed on a dry basis using a Beckman Model 402 hydrocarbon analyzer. A flue gas sample was withdrawn from the stack through an in-stack filter probe and a 15.2 m (50 ft) heat-traced Teflon® sample line. Water was removed using an ice bath and knockout trap. Calibration of the THC analyzer was performed by introducing 0-100 ppm propane standards at the inlet of the heat-traced line.

6.1.2.4 Waste Fuel Sampling

Samples of the waste solvent feed were collected during each test run to provide background information if anomalies arose in the data. A composite of the waste feed was obtained for each test by collecting a minimum of five 125-mL increments over the test period. These 125-mL increments were combined, mixed and stored in glass containers with no headspace. These samples were archived but not analyzed, as no anomalies were encountered in data analysis.

6.2 EXPERIMENTAL DESIGN AND SAMPLE COLLECTION

The test plan approved by EPA for the Semi-VOST field evaluation provided samples for determining: 1) method precision; 2) method bias; 3) breakthrough volumes; and 4) sample stability for selected compounds. Test compounds were selected to provide data on species with different chemical structures, water solubilities, and XAD-2® resin adsorption properties. The experimental design incorporated adequate replication of each type of test to ensure that conclusions or findings would be of known statistical significance.

Sample collection occurred in three separate test series. Each test series and the type and purpose of the samples collected are discussed in the sections below.

6.2.1 Method Precision and Bias

Five tests were performed with the quad-probe to assess method precision and bias. Five deuterated compounds were spiked into the sample trains at the 100 MDL level during the five tests to provide data on precision and bias. During four of the tests, the incinerator feed was also spiked with chlorobenzene and tetrachloroethylene to provide an additional measure of precision.

The samples collected for precision and bias are summarized in Table 2. Sampling conditions and problems encountered are also noted. As shown in this table, all five of the quad-probe tests were conducted over 120-minute sampling periods. The incinerator waste feed solvent was spiked with chlorobenzene and tetrachloroethylene at an amount

TABLE 2. SUMMARY OF TESTS CONDUCTED FOR PRECISION AND BIAS

Test Run[1]	Sample Time (minutes)	Sampling Rate (cfm)[2]	Feed Spike[3]	Deuterated Spike[4]	Applicability for Precision and Bias Determinations
01	120	0.5	Yes	Yes	Trains A, C, D valid for precision and bias based on deuterated pyridine spike only[5]; Train B invalid due to broken probe liner.
02	---	---	---	---	-----
03	120	0.5	Yes	Yes	Trains A, C, and D valid for precision and bias based on deuterated spike; Train B invalidated by sample preparation error.[6]
04	120	0.5	Yes	Yes	All trains valid for precision and bias based on deuterated spike.
05	120	0.5	Yes	Yes	All trains valid for precision and bias based on deuterated spike.
08	120	0.5	No	Yes	Trains A and B valid for precision and bias. Trains C and D used liquid spikes.

---

[1] Test Run 02 was aborted after 30 minutes of sampling due to broken probe liner for Train B. Repair of Train B sheath attempted following this run.

[2] 0.5 ft^3/min is equivalent to 2.36×10^{-4} m^3/s.

[3] Incinerator waste feed spiked with chlorobenzene and tetrachloroethylene.

[4] Five deuterated compounds spiked into sample train with dynamic spiking system.

[5] Trains A, C, and D invalid for other spiked compounds due to sequence of solvent extract concentration by K-D.

[6] Sample went to dryness during K-D concentration.

equivalent to 4 percent by weight during test Runs 01, 03, 04, and 05. This level of spiking was considered by plant personnel to be the maximum safe level for this incinerator.

Overall a total of 17 valid samples was collected for the precision and bias determination. One sample was invalidated due to a broken probe liner (Train B, Run 01).

6.2.2 Breakthrough Volume

Three quad-probe tests were conducted to compare the results of laboratory breakthrough volume studies to data obtained in the field. Conditions for these tests are summarized in Table 3. During these tests, three of the trains were spiked at 100 MDL with the five deuterated compounds and one train was operated unspiked. The three spiked trains provided a triplicate set of samples for the breakthrough analysis and the unspiked train provided a blank or background sample.

Laboratory retention volumes, breakthrough volumes, and breakthrough times for the five compounds are summarized in Table 1. The data in Table 1 indicate that for the 2-hour precision and bias tests discussed in Section 6.2.1, none of the compounds was expected to break through the XAD-2® resin except pyridine. Pyridine is water soluble and would be expected to pass through the resin and be collected in the condensate.

Test Run 06 in Table 3 was conducted over a 3-hour sampling period. This sampling time provided a sample volume that is near the calculated retention volume for toluene, but well below the calculated volumes for chlorobenzene, o-xylene, and tetrachloroethane.

Test Run 10 was conducted over a 6-hour period and provided a sample volume of approximately 5 m^3 (180 ft^3). This sample volume is above the calculated retention volume for toluene but still well below the retention volumes of chlorobenzene, o-xylene and tetrachloroethane.

The final breakthrough test, Run 07, provided a total sample volume of approximately 10 m^3 (360 ft^3), which is greater than the calculated retention volume of chlorobenzene and toluene, but below the calculated retention volumes of tetrachloroethane and o-xylene.

Original plans called for the breakthrough samples to be collected at a sampling rate of 3.54×10^{-4} m^3/s (0.75 cfm) instead of 2.36×10^{-4} m^3 (0.5 cfm). However, operation at the higher sampling rate was

TABLE 3. SUMMARY OF TESTS CONDUCTED FOR BREAKTHROUGH VOLUME

Test Run	Nominal Sample Time (minutes)	Nominal Sampling Rate (cfm)[1]	Average Volume Collected m^3 (cf)	Applicability for Breakthrough Determinations
06	180	0.5	2.67 (94.2)	Trains A, B, and C were dynamically spiked for breakthrough determinations
				Train D was not spiked
10	360	0.5	5.01 (177)	Trains A, B, and C were dynamically spiked and are valid for breakthrough determination
				Train D was not spiked
07	720	0.5	10.05 (355)	Trains A, B, and C were dynamically spiked and are valid for breakthrough determination
				Train D was not spiked

[1] 0.5 cfm is equivalent to 2.36×10^{-4} m^3/s.

not possible due to 1) the excessively high moisture content of the gas stream (>60 percent by volume) and 2) the high ambient temperatures at the test site (~32°C (90°F)). Moisture in the sample is in the vapor phase as it passes through the particulate filter at 120 ± 14°C (250 ± 25°F). This moisture must then be condensed and the gas must be cooled to 20°C (68°F) before it enters the XAD-2® resin trap. At the higher sampling rate, insufficient heat transfer area was available in the condenser to condense the large quantity of water and cool the gas to 20°C. Efforts to increase the water flow through the condenser and to lower the ice bath cooling water temperature by adding salt were unsuccessful. Larger condensers would have been required for operation at the higher 3.54×10^{-4} m^3/s sampling rate.

6.2.3 Sample Stability

Two quad-probe samples (Runs 08 and 09) were collected to provide information on sample stability. Each test was performed over a 2-hour sampling period. Two trains were spiked with the five deuterated compounds using the dynamic spiking system. The other two trains remained unspiked during the flue gas sampling, but were spiked with a liquid containing the same five compounds using a syringe immediately after the sampling. The liquid spiked samples were analyzed with other samples collected during the testing and were used to assess compound loss due to sample transport, preparation and analysis. The dynamically spiked samples were stored for five weeks (Run 08) and nine weeks (Run 09) and then analyzed. Results for the stored samples were compared with those for the liquid spiked samples to assess compound loss due to sample storage.

6.2.4 Spiking System Operating Data

Throughout each run the dynamic spiking system was periodically monitored. A soap film flow meter was used to check the flows of the mass flow controllers prior to testing, during breaks in the testing and at the completion of the testing. Except for Train B, Run 06, the flows varied by less than 3 percent throughout each test. For Train B, Run 06, the variation was 6 percent.

Samples of the spiking gas were obtained from each train at the beginning and completion of each test. The samples were collected with the three-way valve set to exhaust. For each train, a 50-mL gas-tight syringe was used to collect the sample. To ensure that a vacuum was not created and that dilution of the sample did not occur, the sample was withdrawn through a T-connector connected to the valve with a water bubbler attached at one end. The presence of bubbles indicated that sufficient sample was passing the sampling point to provide a representative sample.

The samples were analyzed onsite by GC/FID to verify the concentrations of each of the five spiking components. A cylinder of the five component mix was used as the reference and to verify the stability of the FID. The variance in the FID response is shown in Appendix D. For pyridine, toluene, chlorobenzene, and o-xylene the response varied less than 6 percent from day to day for Runs 04 through 10 (June 20-27). Throughout the day for these four compounds the signal varied less than 10 percent during every run except Run 03 (June 19). For the tetrachloroethane the FID signal varied by 12 percent from day to day and up to 17 percent throughout the day. This larger variation in the tetrachloroethane signal was attributed to two facts:

(1) tetrachloroethane was present in low quantities (less than 10 ppm), and
(2) the tailing of the earlier eluting pyridine interfered with the tetrachloroethane.

The intraday variation for Run 03 (June 19) was quite large (coefficient of variation 30 to 50 percent) because of a GC instrument problem. On Run 03, the heating element for the GC injection loop operated intermittently.

Table 4 lists the percentages of the expected values which were measured for the deuterated compounds. These values were obtained by direct comparison of the area counts of the sample to the area counts of the QC cylinder. GC analysis indicated that the amounts of deuterated pyridine, toluene, and chlorobenzene spiked onto the XAD-2® resin were always within 85 percent of the reported cylinder values during the second week of testing (June 23 to 27) and were usually within 84 percent of the reported values with the exception of chlorobenzene on

TABLE 4. RATIO OF MEASURED CONCENTRATION TO EXPECTED CONCENTRATION FOR DEUTERATED COMPOUNDS

Run Number 01 Date: June 17, 1986

		ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C	Train D
Pyridine	89.2	84.6	94.4	94.2
Tetrachloroethane	55.6	92.8	76.3	90.4
Toluene	88.7	88.7	90.8	89.5
Chlorobenzene	88.2	88.4	91.1	91.9
o-Xylene	83.1	80.1	85.1	83.7

Run Number 03 Date: June 19, 1986

		ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C	Train D
Pyridine	91.0	99.7	91.6	86.0
Tetrachloroethane	147.4[1]	117.8	169.6	131.6
Toluene	90.3	84.3	85.7	85.5
Chlorobenzene	89.9	76.4	80.8	82.2
o-Xylene	83.8	75.1	77.1	77.6

Run Numbers 04 and 05 Date: June 20, 1986

		ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C	Train D
Pyridine	88.0	88.8	85.1	84.9
Tetrachloroethane	74.2	74.3	74.4	71.9
Toluene	95.9	95.6	94.2	94.7
Chlorobenzene	94.2	93.6	88.3	89.4
o-Xylene	87.5	85.7	83.5	81.8

Run Number 06 Date: June 23, 1986

		ppm measured/ppm expected (%)	
Compound	Train A	Train B	Train C
Pyridine	92.0	92.4	93.2
Tetrachloroethane	80.6	80.2	87.8
Toluene	97.2	96.9	98.7
Chlorobenzene	95.3	96.5	100.6
o-Xylene	91.5	93.7	92.4

(continued)

TABLE 4. CONCLUDED

Run Number 07A Date: June 24, 1986

	ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C
Pyridine	100.8	98.6	99.3
Tetrachloroethane	97.0	101.3	96.9
Toluene	98.1	97.9	99.3
Chlorobenzene	95.5	95.4	96.3
o-Xylene	91.6	89.1	88.2

Run Number 07B Date: June 25, 1986

	ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C
Pyridine	92.1	92.5	93.9
Tetrachloroethane	67.1	70.8	72.0
Toluene	93.7	91.9	96.5
Chlorobenzene	86.4	85.3	91.2
o-Xylene	79.2	78.1	79.0

Run Numbers 08 and 09 Date: June 26, 1986

	ppm measured/ppm expected (%)	
Compound	Train A	Train B
Pyridine	95.3	94.7
Tetrachloroethane	74.3	78.3
Toluene	95.5	94.2
Chlorobenzene	94.8	92.3
o-Xylene	86.6	84.7

Run Number 10 Date: June 27, 1986

	ppm measured/ppm expected (%)		
Compound	Train A	Train B	Train C
Pyridine	91.2	91.3	88.1
Tetrachloroethane	86.4	89.0	81.0
Toluene	95.5	95.8	93.8
Chlorobenzene	91.8	92.5	91.2
o-Xylene	84.8	86.0	85.8

---

[1] Instrumental difficulties occurred during this measurement.

June 19, 1986. The measured d_{10}-$\underline{o}$-xylene values ranged from 75 to 94 percent of the cylinder values with the usual range being from 82 to 87 percent. The measured d_2-tetrachloroethane values ranged from 55 to 170 percent of the tank values with the usual range being 77 to 88 percent. On June 19, the temperature of the field GC injection valve decreased during the day. This decrease in temperature may have contributed to the range of the measured values for d_2-tetrachloroethane. However, data were not discarded after the final analysis, since delivery of the deuterated compounds to the sampling trains obviously occurred for all of the test compounds and measured concentrations for test compounds other than d_2-tetrachloroethane were acceptable.

6.2.5 Incinerator Operating Data

Process operating parameters were monitored and/or measured during the testing to document incinerator operating conditions. Data collected for each test run are summarized in Table 5.

6.3 ANALYTICAL PROCEDURES

All samples were prepared according to the Semi-VOST methodology. Numerous extractions were required to accommodate the larger volume (2 to 15 liters) of condensate collected by the sampling trains. The extracts of the condensate for each train were concentrated to approximately 100 mL before being combined with the XAD-2® extract. This sequence of concentration was implemented after Run 01.

A final sample extract volume of 5 mL was delivered for analysis by gas chromatography/mass spectrometry (GC/MS). All samples as received from the field were spiked in the laboratory with surrogate standards prior to any sample preparation. The surrogate compounds were spiked at a level which would be equivalent to 100 times the MDL when the final solvent volume was 5 mL. The surrogate compounds used were the following stable isotopically labeled compounds: d_8-naphthalene, d_5-phenol, d_{10}-ethylbenzene, and d_5-nitrobenzene. These surrogate compounds were used to monitor the efficiency of the sample preparation process for recovering compounds from the matrix. Corrections can validly be made to allow for less than 100 percent recovery of surrogate compounds and the corrected values for the compounds of interest will

TABLE 5. SUMMARY OF INCINERATOR OPERATING CONDITIONS

Test Run No.	Combustion Zone[1] Temperature [°C(°F)]	Stack Gas[1] Oxygen (%)	Stack Gas Temperature [°C (°F)]	Stack Gas Moisture (%)	Carbon Monoxide[1] (ppmv)	Total Hydrocarbons[2] (ppmv)
01	1027 (1880)	5.0	87.8 (190)	62.0	NA[3]	NA[3]
03	1004 (1840)	1.5	87.2 (189)	61.3	55	NA
04	1010 (1850)	2.3	86.7 (188)	56.7	20	NA
05	1016 (1860)	2.2	85.6 (186)	63.4	55	19
06	1010 (1850)	7.0	87.2 (189)	62.2	NA	4.1
07	1021 (1870)	7.5	87.2 (189)	62.7	120	3.0
08	1016 (1860)	7.1	87.8 (190)	64.6	920	70[4]
09	1021 (1870)	7.4	87.8 (190)	63.8	34	13
10	993 (1820)	6.2	87.2 (189)	59.4	200	23

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[1] Data based on plant instrumentation. Average of values recorded at 30- to 60-minute intervals during test period.

[2] Data based on Radian total hydrocarbon analyzer.

[3] Data not available due to instrument malfunction.

[4] Instrument full scale of 100 ppm exceeded during portion of this test run.

then reflect recoveries of surrogates. Measured amounts of test compounds were adjusted by using the ratio of the surrogate recovery of d_{10}-ethylbenzene spiked in the samples to the recovery of this compound from the Research Triangle Institute control samples. A series of control samples prepared by the Research Triangle Institute was analyzed to support Radian analytical data for the Semi-VOST field samples. The Research Triangle Institute prepared control samples on XAD-2® resin which were spiked with the test compounds. The mean recovery values of the deuterated compounds used during the analysis of the control samples were used to adjust the test compound recoveries for the control samples. The same technique for adjustment of values was used for all of the field samples. The collected mass of pyridine was not adjusted because the compound was not retained on the XAD-2® resin, but was collected in the back-half (aqueous) of the Semi-VOST train.

The samples were analyzed on a Finnigan-MAT 5100 GC/MS, using the analytical conditions shown in Table 6. The mass spectrometer was operated in the full scan mode (mass 35 to 450), using electron ionization. The mass spectrometer was tuned to meet EPA criteria for decafluorotriphenylphosphine (DFTPP). DFTPP was analyzed and the tuning criteria were met daily prior to the initiation of any analysis. Since the analyses were directed analyses, identification of compounds of interest was established by direct comparison of analyte chromatographic retention time with the chromatographic retention time of a standard. Comparisons were also made with characteristic ions of the compound present in the analyte at approximately the same ratio as in the standard and with characteristic ions coeluting from the chromatograph.

Immediately prior to analysis, each sample was spiked with a known amount of a mixture of quantitation standards (d_{10}-p-xylene, d_5-bromobenzene and, if late-eluting compounds were observed, d_{10}-phenanthrene). The response ratio for the quantitation standard relative to the compounds of interest in a sample was then compared to a similar ratio established from the analysis of calibration standards. The response factor calibration for the individual compounds was established by using a five-point calibration curve with compound levels ranging from 25 to 200 ug/mL. Sample concentrations were adjusted to fit within this range wherever possible. However, the dynamic range of materials encountered

TABLE 6. ANALYTICAL CONDITIONS USED FOR ANALYSIS OF SEMI-VOST FIELD SAMPLES

Instrument	Finnigan-MAT 5100 GC/MS/DS
Column	30 meter 0.32 mm I.D. DB-5 fused silica capilary
Emission Current	0.50 mA
Electron Energy	11.22 aJ (70 eV)
Manifold Temperature	80°C
GC Program	35°C (4.0 min) - 270°C, 10°C/min and hold
Interface Oven Temperature	280°C
Injector Temperature	280°C
Column Head Pressure	55.2 kPa (8 psi)
Carrier Gas	Helium
Carrier Gas Flow	1.0 mL/min
Injection Mode	Splitless for 0.6 min, then 10:1 split
Scan Range	35 to 450 daltons
Total Scan Time	0.921 sec

in the samples was such that sometimes not all of the compounds present in the sample could be adjusted to fit within the calibration range simultaneously. For the compounds for which an appropriate adjustment was not possible, an extrapolation was performed. The validity of this extrapolation was verified by dilution for two samples.

The method described in the Semi-VOST protocol for determining response factors, with subsequent quantitative calculations for compounds of interest, was used for calculating quantities for all compounds except tetrachloroethane. In the case of tetrachloroethane, all quantities observed were very low and were not quantitated well by the entire calibration curve. As a result, a mean response factor for the lowest (and therefore closest) value of the calibration curve was used to calculate the quantity of tetrachloroethane.

All samples were examined for the presence of native chlorobenzene and tetrachloroethylene. These compounds had been spiked into the feed to allow another measure of method precision. These compounds were not found in the collected emission sample, either in the original 5 mL sample extract or in extracts which were concentrated fivefold. Solvent spiked with chlorobenzene and tetrachloroethylene was concentrated and analyzed to demonstrate that the compounds of interest were not being lost during concentration. Since the level of efficiency of the combustion process was sufficient to preclude observation of the compounds in the emissions, chlorobenzene and tetrachloroethylene could not be used to measure method precision.

Supporting Quality Control/Quality Assurance data are presented in Appendix E. Surrogate compound recoveries are summarized in Table 7. Results of the analysis of the Research Triangle Institute control samples are summarized in Table 8.

6.4 RESULTS AND DISCUSSION

6.4.1 Precision and Bias

Table 9 summarizes the results of precision and bias determinations. Bias was calculated relative to percent recovery of the spiked compound, and precision in terms of standard deviations and percent coefficients of variation of the percent recoveries for each spiked compound. The bias ranged from -29.0 percent for d_5-pyridine to

TABLE 7. OVERALL SURROGATE RECOVERIES FROM ALL MEDIA, OVER ALL RUNS

Surrogate Compound	Mean Recovery, %[1]	Coefficient of Variation, %
d_{10}-ethylbenzene	58	41
d_5-phenol	70	29
d_5-nitrobenzene	81	35
d_8-naphthalene	78	41

[1] Mean of 50 values; no data points discarded.

TABLE 8. RESULTS OF ANALYSIS OF RTI CONTROL SAMPLES

Compound	Expected Level, ug	Determined Levels, ug[1] (1)	(2)	(3)	Mean Observed Level (ug/module)	% bias
Pyridine	1,963.8	1924	1942	1905	1,923.7	-2.04
Toluene	866.9	850	822	824	832.0	-4.03
Chlorobenzene	221.1	216	214	221	217.0	-1.84
1,1,2,2-Tetrachloroethane	159.5	146	147	143	145.3	-8.90
o-Xylene	880.2	818	829	820	822.3	-6.50
Dodecane	748.8	---	---	---	---	---
					Overall Average % Bias	-4.68

[1] Values corrected for Surrogate Recovery.

[2] $\% \text{ Bias} = \frac{\text{mean observed} - \text{Expected Level}}{\text{Expected Level}} \times 100$

-0.9 percent for d_{10}-o-xylene. Pyridine was the only compound tested which has significant water solubility. Because of the high moisture content of the stack gases, several liters of water condensate were extracted for preparation of the samples. Recovery of a water-soluble compound is far less efficient when it must be extracted from a large volume using multiple extraction and concentration steps. An analysis of variance of compound recovery showed the mean percent recoveries were not equal at a level of significance less than 0.005. Method bias, therefore, was compound specific, or at least specific by classes, e.g., water-soluble.

Precision in terms of percent coefficient of variation ranged from 8.1 percent for d_{10}-o-xylene to 32.9 percent for d_2-tetrachloroethane. A Bartlett Test[8] for homogeneity of compound variances of percent recovery showed that there was essentially zero probability that the compound variances were equal. From the results of this study it was not possible to give an overall, or pooled, variance, standard deviation, or coefficient of variation for all compounds tested. Rather, it must be concluded that the precision was compound specific. The percent coefficient of variation for d_5-pyridine was not significantly different from that of d_8-toluene or d_5-chlorobenzene for these three compounds, as the precision did not seem to be related to the water-solubility characteristics.

Table 10 gives precision and bias results for the five spiked compounds used in this study, d_5-pyridine, d_8-toluene, d_5-chlorobenzene, d_{10}-o-xylene, and d_2-tetrachloroethane, respectively. The tables show the run number, the number of valid samples for each run, mean percent recoveries, standard deviations, and percent coefficients of variation. Overall figures shown on the bottom row of each table give the total number of samples, the weighted mean percent recovery for each compound, and pooled standard deviations and coefficients of variation.

The Box modification[8] of the Bartlett Test for homogeneity of variances indicated that, for each compound, there was no difference in the variances of the percent recoveries for the runs listed in Table 10. It is therefore appropriate to use the pooled standard deviations for each compound to characterize the precision of the percent recovery measurement.

TABLE 9. SUMMARY OF PRECISION AND BIAS RESULTS

Compound	Number of Valid Samples	Mean % Recovery	Percent Bias[3]	Precision: Standard Deviation	Precision: Percent Coefficient of Variation
d_5-pyridine	16[1]	71.0	-29.0	12.6	17.7
d_8-toluene	13[2]	85.1	-14.9	12.4	14.6
d_5-chlorobenzene	13	86.2	-13.8	11.8	13.7
d_{10}-o-xylene	13	99.1	-0.9	8.0	8.1
d_2-tetrachloroethane	13	81.5	-18.5	26.8	32.9

[1] Run 03B samples went to dryness in preparation; data were discarded.

[2] Runs 01A, 01C, and 01D were discarded because of the sequence of extractions and concentrations. For all of the remaining samples, the Soxhlet extract of the XAD-2® was the final aliquot concentrated.

[3] Percent bias = Mean % recovery-100

TABLE 10. PRECISION AND BIAS RESULTS

d_5-Pyridine

				Precision	
Run	Number of Valid Samples	Mean % Recovery	Percent Bias	Standard Deviation	Percent Coefficient of Variation
01	3	76.3	-23.7	17.1	22.4
03	3	83.4	-16.6	5.1	6.1
04	4	60.8	-39.2	4.2	6.9
05	4	72.5	-27.5	18.1	25.0
08	2	62.1	-37.9	11.1	17.9
Overall	16	71.0	-29.0	12.7	17.7

d_8-Toluene

				Precision	
Run	Number of Valid Samples	Mean % Recovery	Percent Bias	Standard Deviation	Percent Coefficient of Variation
03	3	84.2	-15.8	5.6	6.7
04	4	76.3	-23.7	5.6	7.3
05	4	88.7	-11.3	18.6	21.0
08	2	96.9	-3.1	2.9	3.0
Overall	13	85.1	-14.9	12.4	14.6

d_5-Chlorobenzene

				Precision	
Run	Number of Valid Samples	Mean % Recovery	Percent Bias	Standard Deviation	Percent Coefficient of Variation
03	3	88.7	-11.3	8.4	9.5
04	4	83.9	-16.1	14.9	17.8
05	4	93.9	-6.1	12.9	13.7
08	2	96.9	-3.1	1.9	2.0
Overall	13	86.2	-13.8	11.8	13.7

(continued)

TABLE 10. CONCLUDED

d_{10}-o-Xylene

Run	Number of Valid Samples	Mean % Recovery	Percent Bias	Precision	
				Standard Deviation	Percent Coefficient of Variation
03	3	100.3	+0.3	7.7	7.7
04	4	98.0	-2.0	11.7	11.9
05	4	98.7	-1.3	8.8	8.9
08	2	100.4	+0.4	1.2	12.0
Overall	13	99.1	-0.9	8.0	8.1

d_2-Tetrachloroethane

Run	Number of Valid Samples	Mean % Recovery	Percent Bias	Precision	
				Standard Deviation	Percent Coefficient of Variation
03	3	48.8	-51.2	8.5	17.4
04	4	97.0	-3.0	25.3	26.1
05	4	75.9	-24.1	13.1	17.3
08	2	110.8	+10.8	5.4	4.9
Overall	13	81.5	-18.5	26.8	32.9

An analysis of variance (ANOVA) for each compound (Table 10) showed that, except for d_2-tetrachloroethane, the mean recovery was not different for the six runs tested. The percent recovery was therefore not a function of the run conditions. For the case of d_2-tetrachloroethane, the mean percent recoveries were not equal, at the 0.05 level of significance, and ranged from 48.8 percent to 110.8 percent. The results from Run 03 (48.8 percent recovery) have been identified as a particularly low value, possibly because of the range in the field determination of quantity delivered. No determinate problem has been identified to justify exclusion of this value from the data set. The weighted mean percent recoveries for each compound were therefore used to estimate the method bias.

6.4.2 Results of Distributive Volume Experiments

Before breakthrough volume is reached, a linear relation (through the origin) exists between amount of organic compound adsorbed and sample volume. The data of Table 11 were tested to determine if the breakthrough volume had been reached using an F statistic which measured the lack of fit of the data to a straight line through the origin. If there were no lack of fit, the breakthrough volume had not been reached. If there were a lack of fit to the linear relationship the breakthrough volume had been exceeded.

A series of distributive volume experiments using three quad probe runs was conducted to compare the laboratory determinations of retention volumes to field determinations. Table 11 presents the distributive volume data generated from the field test. These data were used to develop Figures 5 through 8. Figures 5 through 8 show the results of the distributive volume experiments for the spiked compounds d_8-toluene, d_5-chlorobenzene, d_{10}-*o*-xylene and d_2-tetrachloroethane, respectively. The data analysis was done in the following way.

For d_8-toluene and d_5-chlorobenzene the adsorption, sample-volume data were divided into two groups --- first, only those data up through 5.05 m^3; and second, all the data through 10.14 m^3. For each of the compounds and data groups, a linear regression through the origin was done. Then F tests were done to determine if there were significant lacks of fit of the data.

TABLE 11. DISTRIBUTIVE VOLUME, ADSORPTION RESULTS

Sample Volume m^3	Adsorbate			
	d_8-toluene ng	d_5-chlorobenzene ng	d_{10}-o-xylene ng	d_2-tetrachloroethane ng
1.66	934	174	937	94
1.64	954	173	924	92
2.66	1291	323	1315	192
5.05	2297	632	2764	291
5.00	1698	553	2553	290
5.00	2071	615	2805	270
9.98	3041	781	6908	492
10.04	1698	647	5584	530
10.14	2037	607	4737	462

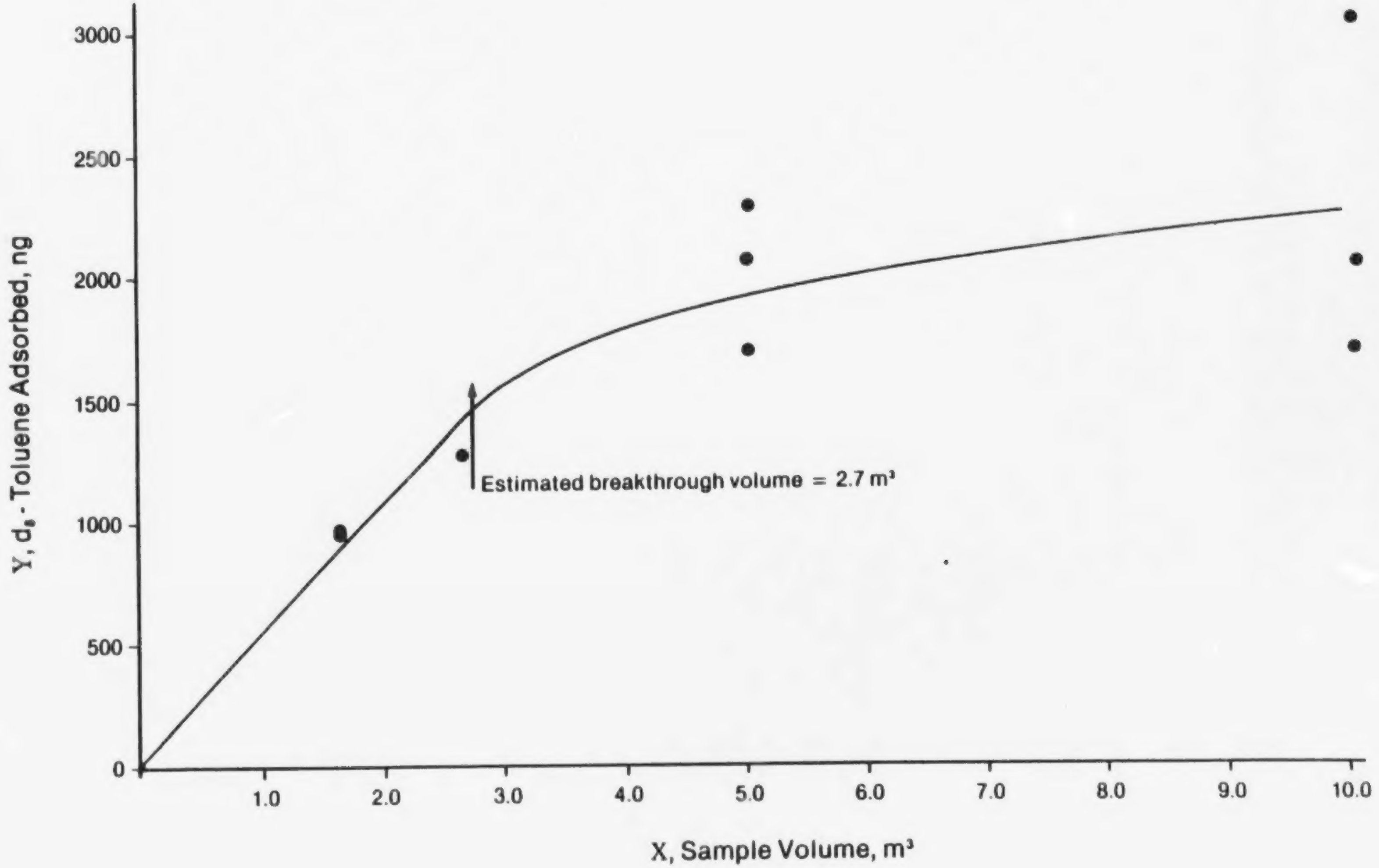

Figure 5. Distributive Volume Studies for d_8 - Toluene

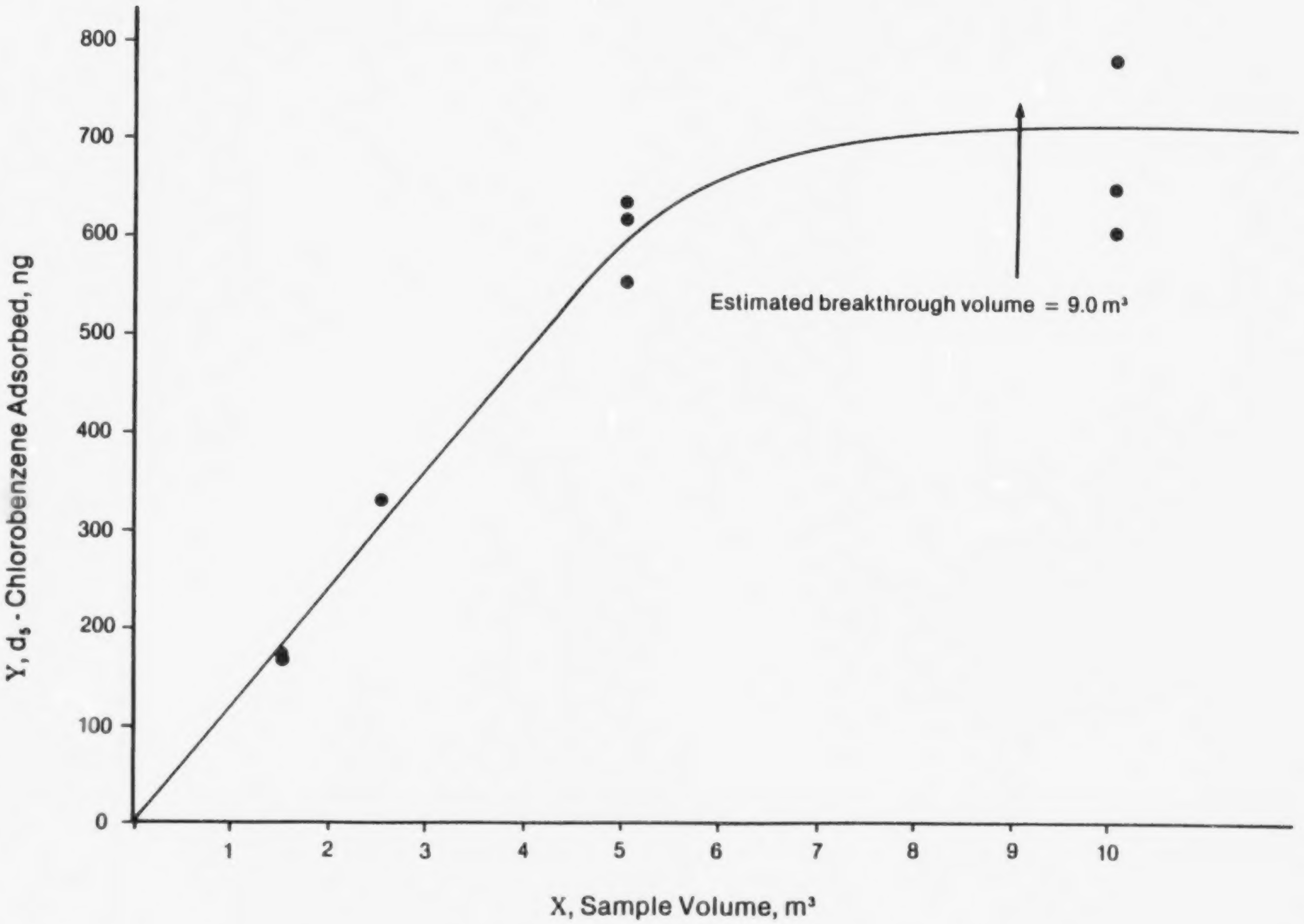

Figure 6. Distributive Volume Studies for d_5 - Chlorobenzene

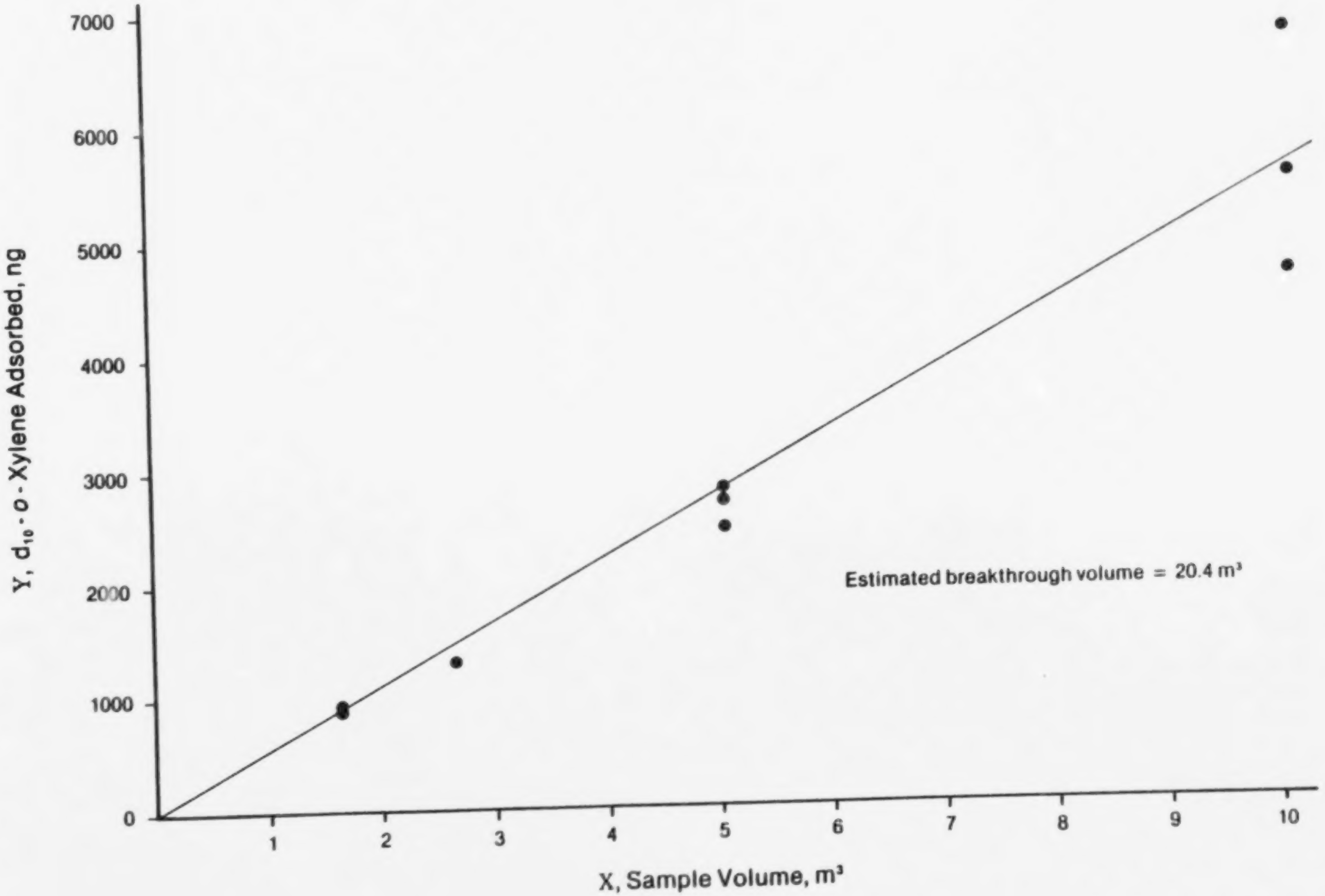

Figure 7. Distributive Volume Studies for d_{10}-*o*-Xylene

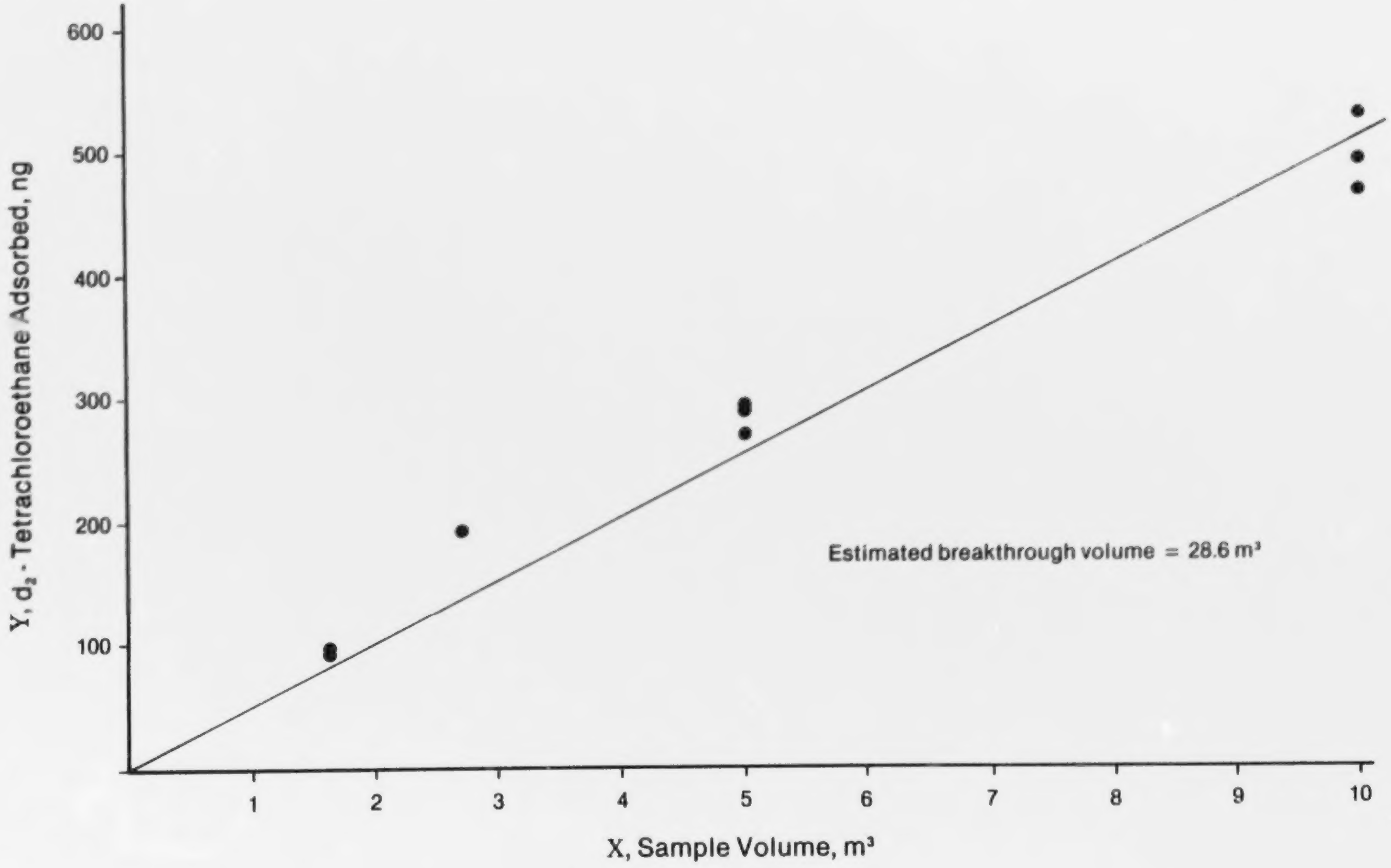

Figure 8. Distributive Volume Experiment for d_2 - Tetrachloroethane

The regression equation is:

$$Y = b_1X$$

where

Y = the expected value of nanograms adsorbed,

b_1 = the regression constant, and

X = sample volume, m^3

Table 12 shows the results of the statistical analyses for the selected data groups. Regression constants, b_1, are given for each data group, and are the slopes of the regression lines through the origin. The F statistics in Table 12 estimate the lack of fit of the data relative to the precision of a data set at a particular volume (i.e., "pure error"). In the case of d_8-toluene and the data group to 5.0 m^3, the lack-of-fit F statistic is 0.720 while the critical F for the appropriate degrees of the freedom and 0.05 level of significance is 16.0. Because the calculated F statistic is less than the critical F, the conclusion is that a linear fit is appropriate for the data.

Applying the same test to the second data group (through 10.0 m^3 sample volume) produces a lack-of-fit F statistic of 44.6 for d_8-toluene which is greater than the critical F of 7.76 at the 0.05 level of significance. Thus, a significant lack of fit is apparent for the second set of data up through 10 m^3. Once breakthrough has occurred, the adsorbate-vs.-sample volume relationship is no longer linear because it will level off to an equilibrium adsorbed concentration. These results indicate that the breakthrough volume occurred before 10 m^3. If the first data set up to 5.0 m^3 sample volume is taken to be linear (through the origin), then the breakthrough volume was greater than 5.0 m^3.

During the laboratory phase of the testing program, estimates of the breakthrough volume, measured by the frontal elution technique, indicated that for toluene, breakthrough was expected to occur at about 2.7 m^3 for the sampling conditions used in the field test. A straight line from that point through the origin is shown in Figure 5. After that point as the sample volume was increased, a curved line was drawn

TABLE 12. DISTRIBUTIVE VOLUME RESULTS FOR BREAKTHROUGH STUDIES

Compound	Results Through 5 Cubic Meters		Results Through 10 Cubic Meters	
	b_1	F^1	b_1	F^1
d_8-toluene	420.27	0.720	268.49	44.6
d_5-chlorobenzene	118.87	0.327	79.00	14.8
d_{10}-o-xylene	--	--	563.22	0.1977
d_2-tetrachloroethane	--	--	51.13	4.143

[1] For the results through 5 cubic meters, if $F \leq F_{2,3,0.95}$ (=16.0), then there is no lack of fit.

For the results through 10 cubic meters, if $F \leq F_{3,5,0.95}$ (=7.76) then there is no lack of fit.

which would follow the expected pattern of departure from linearity after breakthrough, approaching an asymptotic value beyond 10 m^3.

Results similar to those for d_8-toluene are shown for d_5-chlorobenzene in Figure 6 and Table 12. The data up through 5.0 m^3 show no lack of fit for the linear relation through the origin, while the data through 10 m^3 show a lack of fit. The laboratory tests for chlorobenzene estimated the retention volume to be 9.0 m^3, consistent with the data of Figure 6. Figure 6 suggests that the breakthrough volume for d_5-chlorobenzene was closer to 5.0 m^3, than to the laboratory determined retention volume.

Distributive volume data for d_{10}-o-xylene and d_2-tetrachloroethane are plotted in Figures 7 and 8. Both show good linearity through 10 m^3, indicating that no breakthrough occurred up to that sample volume. Table 12 confirms that there is no lack of fit from the linear relation through the origin. The laboratory studies estimated breakthrough volumes for these compounds to be 20.4 m^3 and 28.6 m^3, respectively. Figures 7 and 8 support these estimates (at least up to 10 m^3). The use of gas chromatography retention volume measurements to estimate the maximum sample volume that may be employed in field testing is a technique that has been used widely in stack sampling for organic compounds. In the present study, field data for chlorobenzene and toluene show that breakthrough occurred at approximately the volumes predicted by the laboratory studies. Further, the laboratory results also indicated that tetrachloroethane and xylene would not break through within the volumes samples in the field study, and no breakthrough was observed. Thus, these data support the conclusion that estimating breakthrough volumes by gas chromatography is a viable technique for selecting sampling times and flow rates when sampling with XAD-2®-filled cartridges.

No adsorption data are plotted for d_5-pyridine because for the distributive volumes used in the field test, about 88 percent of the d_5-pyridine was found in the water impingers following the XAD-2® adsorption bed. These results show that breakthrough had occurred, confirming the laboratory measurements which estimated breakthrough to be no higher than 1.4 m^3. Figure 9 shows the percent collection based on amount spiked of d_5-pyridine in the back half of the Semi-VOST train, indicating that the breakthrough volume was less than the sample volumes collected in the field test. This result was expected based on the laboratory studies. Pyridine forms an organic chloride salt in the presence of aqueous hydrochloric acid. This organic chloride salt is highly water soluble. The salt would therefore pass through the resin bed in the water phase and be collected primarily in the back-half of the Semi-VOST train.

6.5 STABILITY STUDIES

Field Test Runs 08 and 09 were 2-hour runs designed to test the stability of the XAD-2® samples during the time between sampling and analysis. The percent recoveries of the deuterated spiked for each sampling train are given in Table 13. Trains A and B were dynamically spiked, while Trains C and D were spiked with a liquid spike containing an identical quantity of the deuterated compounds.

The necessary steps in the analysis include sampling, addition of surrogate compounds, extraction of the sample resin, and analysis of the extract. Table 14 lists the number of days between sampling and extraction, extraction and analysis, and sampling and analysis. The latter figure, the number of days between sampling and analysis, is the sum of the first two figures.

Comparisons were made between the data sets for Runs 08 and 09 to give more insight on the stability with time of deuterated organic compounds on XAD-2® resin. The mean percent recoveries for the liquid spikes on Trains C and D for Run 08 were compared to the mean percent recoveries for Trains C and D for Run 09. Student's t statistic was calculated for each deuterated compound; the results are shown in Table 15. The t test checked the null hypothesis that the mean percent recoveries were equal. The critical value of Student's t at two degrees of freedom is 4.303 at a level of significance of 0.050. If the calculated t value is greater than the critical Student t's, the conclusion is that the mean percent recoveries are not equal. The

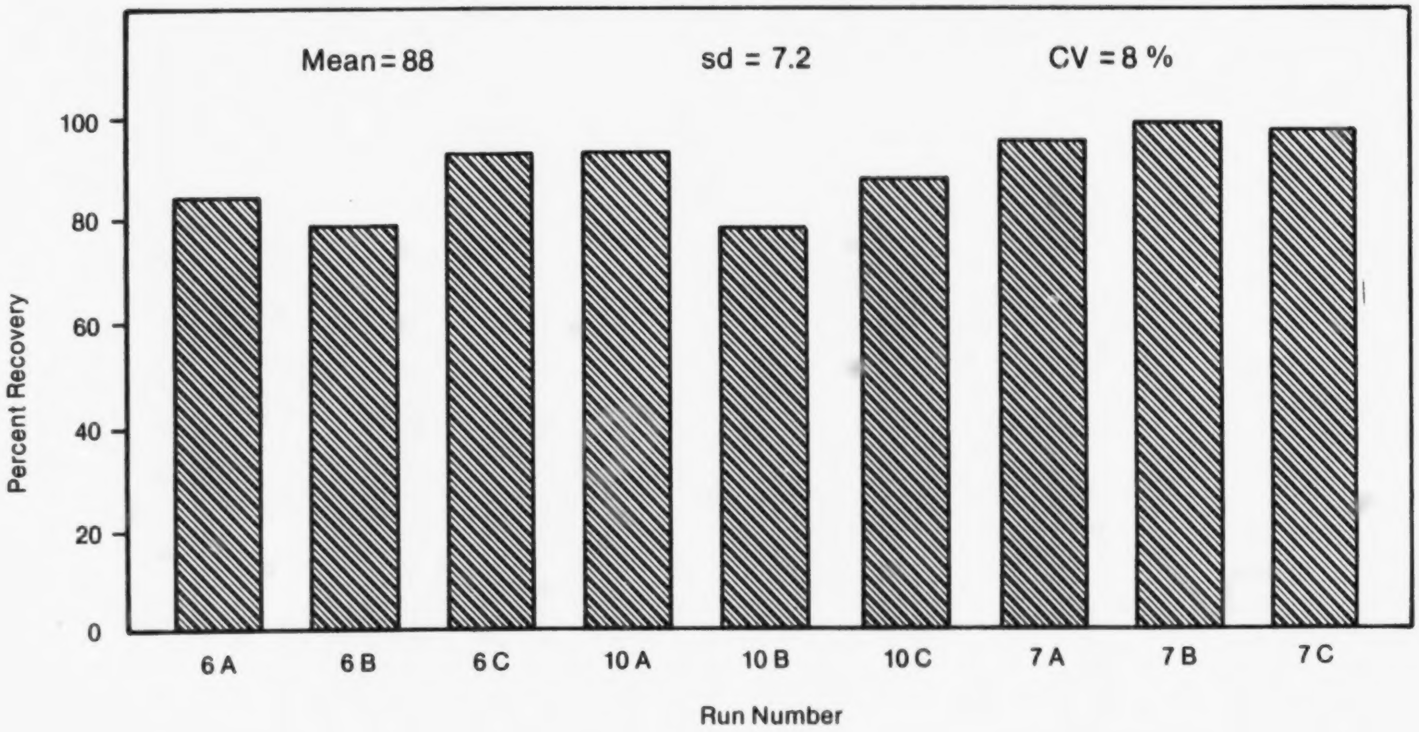

Figure 9. Percent Collection d5 - Pyridine Back - Half of Semi - VOST Train

TABLE 13. SEMI-VOST FIELD TEST PERCENT RECOVERY RESULTS

	Run 08			
	Dynamic Spike		Liquid Spike	
Compound	Train A	Train B	Train C	Train D
d_5-pyridine	54.3	69.9	104.3	104.9
d_8-toluene	94.8	99.0	111.6	112.9
d_5-chlorobenzene	95.6	98.3	85.9	100.0
d_{10}-*o*-xylene	99.7	101.2	97.2	98.9
d_2-tetrachloroethane	114.6	107.0	86.1	91.1

	Run 09			
	Dynamic Spike		Liquid Spike	
Compound	Train A	Train B	Train C	Train D
d_5-pyridine	84.0	100.2	94.4	85.6
d_8-toluene	78.5	85.0	67.1	70.9
d_5-chlorobenzene	91.8	94.3	63.3	70.4
d_{10}-*o*-xylene	106.3	107.1	77.7	79.8
d_2-tetrachloroethane	143.9	134.9	55.4	82.2

TABLE 14. TIME INTERVAL (DAYS) BETWEEN SAMPLING, EXTRACTION, AND ANALYSIS

Run No.	Sampling and Extraction				Extraction and Analysis				Sampling and Analysis			
	A	B	C	D	A	B	C	D	A	B	C	D
08	35	35	46	46	13	13	18	18	48	48	64	64
09	63	63	46	46	1	1	18	18	64	64	64	64

TABLE 15. SEMI-VOST t-STATISTICS COMPARING RUNS 08 AND 09

Compound	t (1)[1]	t (2)[2]	t (3)[3]	t (4)[4]
d_5-pyridine	-2.668	-5.445	0.228	3.311
d_8-toluene	3.915	-6.983	3.387	21.538
d_5-chlorobenzene	2.120	0.557	6.961	3.307
d_{10}-*o*-xylene	-7.353	2.117	24.875	14.287
d_2-tetrachloroethane	-4.856	4.881	4.995	1.453

[1] Compares means of Test 08, A and B with mean of Test 09, A and B.

[2] Compares means of Test 08, A and B with mean of Test 08, C and D.

[3] Compares means of Test 09, A and B with mean of Test 09, C and D.

[4] Compares means of Test 08, C and D with mean of Test 09, C and D.

statistical analyses in Table 15 show that:

- The two sets of dynamic spiking data (Runs 08A, 08B *vs*. 09A, 09B, column under t (1)) show significant differences for d_{10}-*o*-xylene and d_2-tetrachloroethane.

- Recoveries obtained from dynamic spiking (Runs 08A, 08B) are significantly different from recoveries obtained from liquid spiking (Runs 9C, 9D) for all compounds except d_5-pyridine and d_8-toluene (column under t (3)).

- The two sets of liquid spiking data (Runs 08C, 08D and 09C, 09D) show significant differences between mean percent recoveries obtained for d_8-toluene and d_{10}-*o*-xylene (column under t (4)); all other compounds show no significant difference.

The difference in holding time before extraction for dynamically spiked XAD-2® samples (35 days for Run 08A and B, 63 days for Run 09A and B) showed significant differences for only d_{10}-*o*-xylene and d_2-tetrachloroethane. The mean recovery for d_2-tetrachloroethane was 139.4 and 110.8 percent for Runs 09A and B and Runs 08A and B, respectively. These data indicate a problem for this compound since recovery above 100 percent is chemically unrealistic. Therefore, these data for d_2-tetrachloroethane should be discounted in the comparison of holding times. For d_{10}-*o*-xylene the precisions for Runs 08A and B and Runs 09A and B are relatively small (1.05 and 0.53% CV, respectively). Chemically, there is no significance to a range of recovery between 100 and 110 percent, so the d_{10}-*o*-xylene should not be included in the same population as d_2-tetrachloroethane.

For d_5-pyridine, d_8-toluene and d_5-chlorobenzene there was no significant difference between the mean percent recovery for holding times (between sampling and analysis) of 35 and 63 days. The data for d_2-tetrachloroethane showed chemically unrealistic results. The statistical analysis of the data for d_{10}-*o*-xylene at the two different holding times leads to the conclusion that there is a significant difference. However, a chemical examination of the four values for recoveries (99.7, 101.2, 106.3, and 107.1 percent) leads to the conclusion that these recoveries are not different. The overall conclusion is that the holding time (up to 63 days) between sampling and analysis does not significantly affect the results obtained.

Greater variation was encountered, in the field study reported here, between different sets of recoveries obtained from duplicate liquid spiking experiments than when two sets of recoveries obtained from dynamic spiking were compared or when dynamic spiking was compared to liquid spiking.

SECTION 7

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APPENDICES

APPENDIX A

SAMPLING AND ANALYSIS PROCEDURES FOR THE DETERMINATION OF SEMI-VOLATILE COMPOUNDS FROM COMBUSTION SOURCES

INTRODUCTION

Appendix A is the draft of the semi-VOST sampling and analysis method. With the exception of typographical errors and editorial comments, all changes and additions to the draft method submitted as Appendix A in the interim final report "Laboratory and Field Evaluation of the Semi-VOST Method," Volume II, PB86 123569112, September 5, 1985, are listed below with the corresponding section and appendix in which the changes or additions occur.

Section 4.3.3

The following sentences have been added:

- Begin the extraction immediately after completing the assembly of the apparatus.

- Separate out any water present in the extract and add it to the condensate.

- If water soluble compounds are being analyzed and if it has been shown that the compounds are not extracted efficiently with methylene chloride, extract the XAD-2® resin a second time with methanol.

Appendix A-4

A screening procedure for water soluble compounds has been added to the Semi-VOST method and is presented in Appendix A-4.

SAMPLING AND ANALYSIS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high efficiency glass or quartz fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic ladden particulate materials, and the porous, polymeric resin to adsorb semi-volatile organic species. Semi-volatile species are defined as compounds with boiling points greater than 100°C.

Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

1.2 Applicability. This method is applicable to the determination of the Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHC's) from incineration systems.[1] This method also may be used to determine particulate emission rates from stationary sources per U.S. EPA Method 5.[2]

1.3 Method Detection Limit. The overall method detection limits (lower and upper) must be determined on a compound by compound basis as different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). Also, the method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (break-through).

1.4 Method Precision and Bias. The overall method precision and bias must be determined on a compound by compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collect, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13 and -16 percent have been determined for toluene and 1,1,2,2-tetrachloroethane,. respectively. A method precision of 19.9 percent was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semi-VOST trains sampling the emissions from a hazardous waste incinerator.

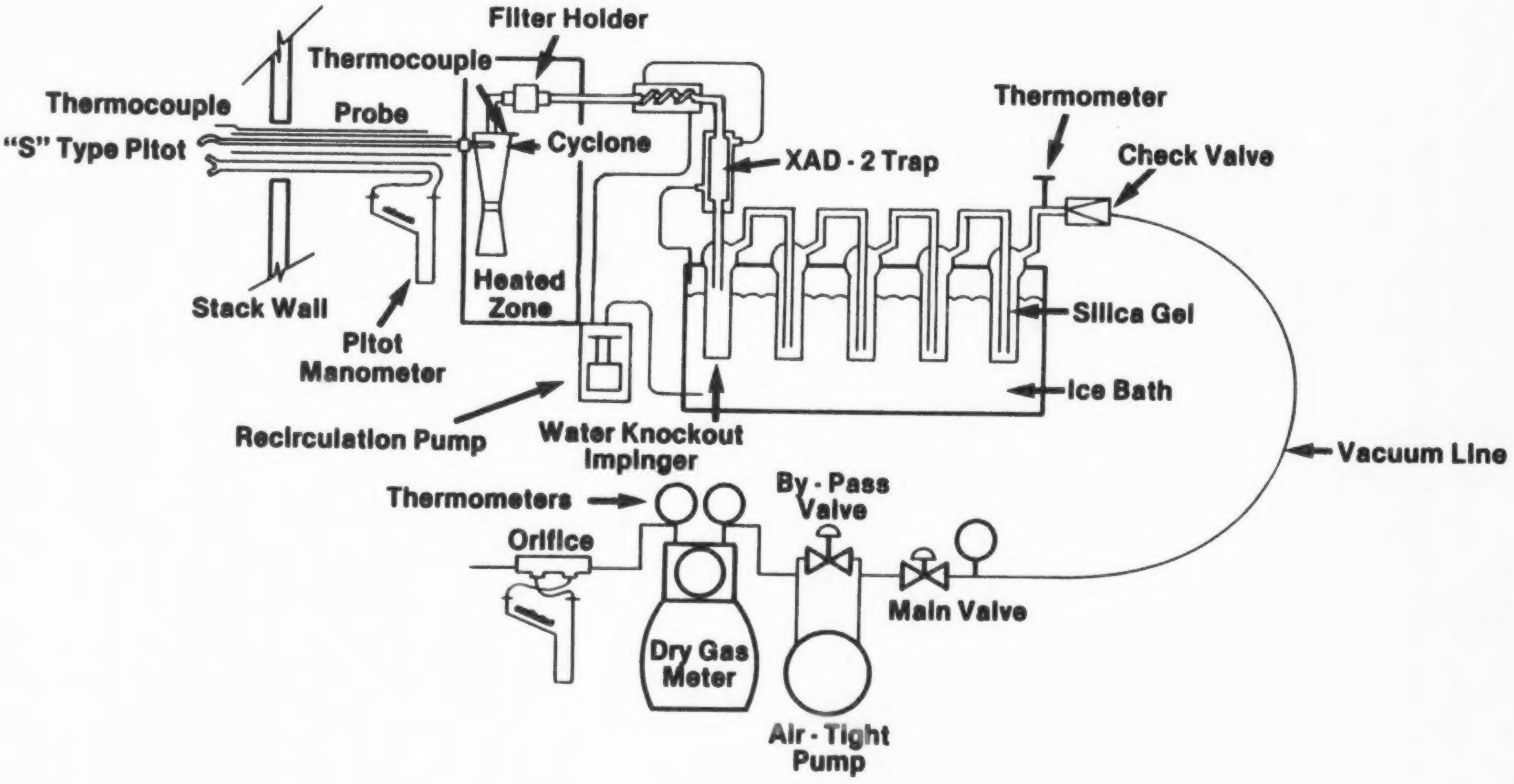
1.5 Interferences. Oxides of nitrogen (NO_x) are possible interferents with the determination of certain water soluble compounds such as dioxane, phenol, and urethane. These compounds may react with NO_x in the presence of moisture and, therefore, reduce their concentration. Other areas of concern which could result in a positive or negative bias are (1) compound stability in methylene chloride, (2) the formation of water soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These topics should be addressed on a compound by compound basis before using this method.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 2-1. This sampling train configuration is adapted from EPA Method 5[2] procedures and most of the equipment required is identical to that used in EPA Method 5 determinations. The additional components required are a condenser coil and a sorbent module, which is used to collect semi-volatile organic materials that pass through the glass or quartz fiber filter in the gas phase.

Construction details for the basic train components are given as part of EPA Method 5 in the report by Robert M. Martin;[5] commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. In addition, the following subsections list changes to the basic system described by Martin, and identify allowable train modifications.

Basic operating and maintenance procedures for the sampling train are described by Jerome J. Rom.[6] As correct usage is important in obtaining valid results, all users should refer to this reference and adopt the operating and maintenance procedures outlined therein, unless otherwise specified. The sampling train consists of the components described in the following paragraphs.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Thermocouple
Thermocouple
Probe
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Cyclone
XAD - 2 Trap
Thermometer
Check Valve
Stack Wall
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Heated
Zone
Silica Gel
Ice Bath
Recirculation Pump
Water Knockout
Impinger
Vacuum Line
Thermometers
By - Pass
Valve
Orifice
Main Valve
Dry Gas
Meter
Air - Tight
Pump

Figure 4 - 1. Semi - VOST Sampling Train

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant inside diameter (ID). The probe nozzle shall be the buttonhook or elbow design, unless another configuration is necessary for a special application. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be considered for particular applications.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) inside diameter. If higher volume sampling trains are used, nozzles with ID's increasing in increments of 0.16 cm (1/16 in.) can be procured. Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate glass or quartz tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F), or such other temperature appropriate for a particular application. Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to Martin[5] and utilizing the calibration curves of Rom[6] (or calibrated according to the procedure outlined in Rom) are considered acceptable.

Either borosilicate glass or quartz probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1,650°F). Water-cooling of the stainless steel sheath will be necessary, however, at temperatures approaching and exceeding 500°C.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of EPA Method 2[2] or other appropriate[7] devices. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity head (ΔP) readings, and the other for orifice differential pressure (ΔH) readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of material(s) that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon® or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The filter holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) in the vicinity of the filter holder during sampling; other temperatures may be appropriate for particular applications.

2.1.7 Organic Sampling Module. This unit consists of three sections including a gas conditioning section, a sorbent trap and a condensate knockout trap. The gas conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 grams of porous polymeric resin (Rohm and Haas XAD-2®). The most commonly used coolant is ice water from the impinger ice water bath constantly circulated through the outer jacket using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate vertically downward from the conditioning section, through the adsorbent medium, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon® or other inert materials.

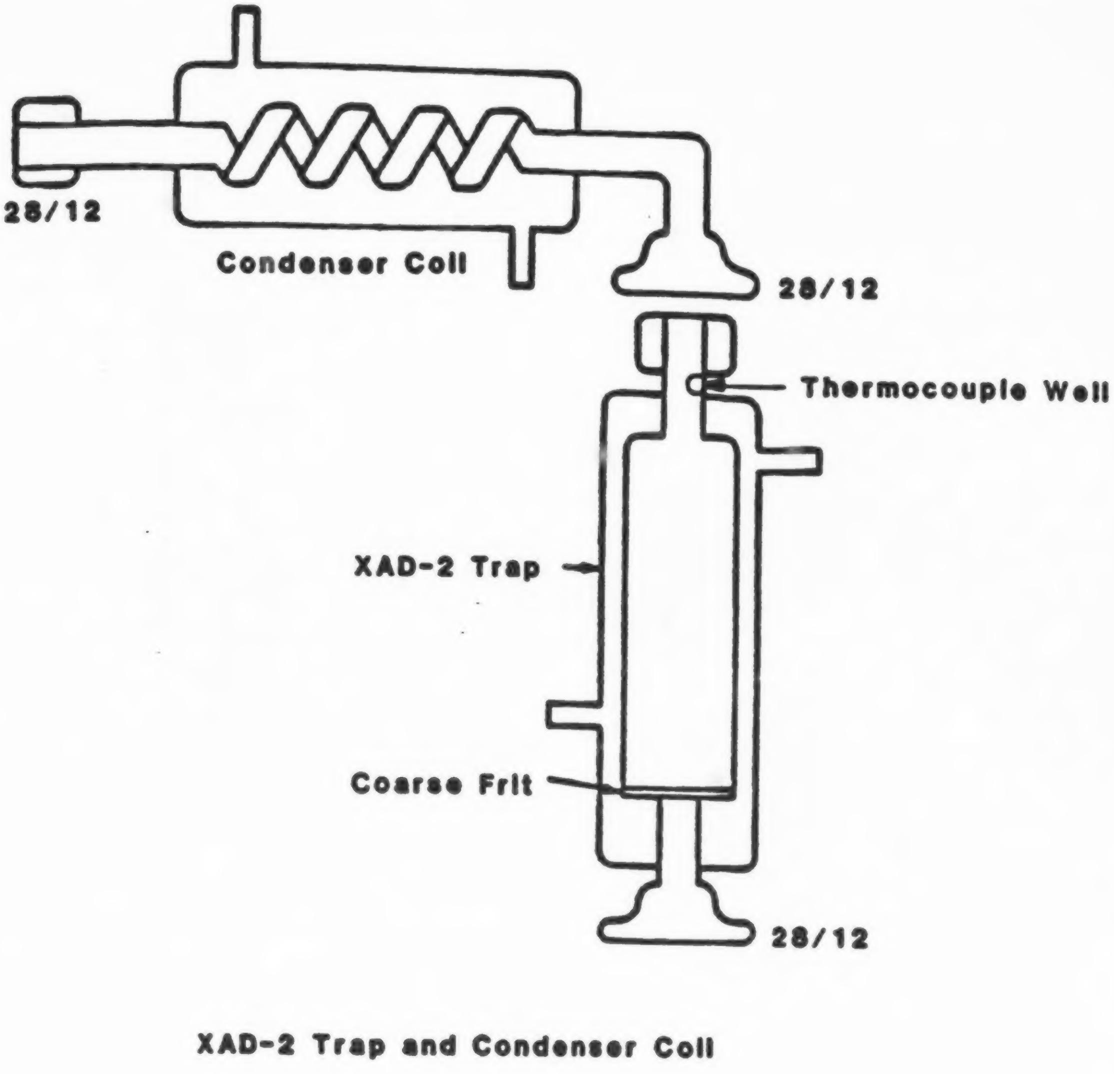
Versions of the complete organic module are not commercially available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2-2 and 2-3. (The thermocouple well is shown in Figure 2-2).

2.1.8 Impinger Train. The following system shall be used to determine the stack gas moisture content. Following the knockout trap are four 500 mL impingers connected in series with leak-free ground glass joints. The first, third and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm. (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or be charged with a caustic solution should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

2.1.9 Metering System. The necessary components are a vacuum gauge, a leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), and a dry gas meter capable of measuring volume to within 1 percent, as shown in Figure 2-1. At a minimum, the pump should be capable of 4 cfm free flow and the dry gas meter should have a recording capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 1 percent may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

Sampling trains utilizing metering systems designed for higher flow rates than those described by Martin[5] or Rom[6] may be used provided that the specifications of this method are met.

2.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm. Hg (0.1 in. Hg). The barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric



28/12
Condenser Coil
28/12
Thermocouple Well
XAD-2 Trap
Coarse Frit
28/12
XAD-2 Trap and Condenser Coil

Figure 2-2. Acceptable sorbent module design #1.

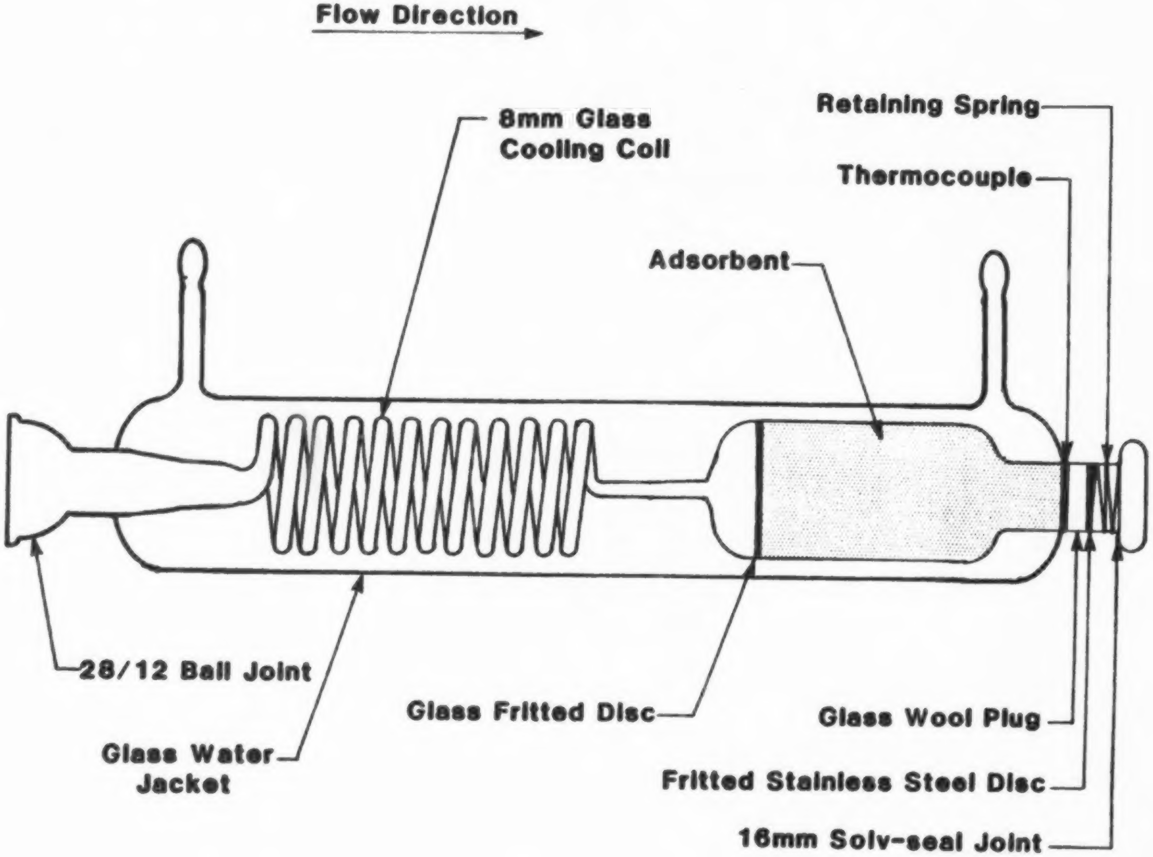

Flow Direction
8mm Glass Cooling Coil
Retaining Spring
Thermocouple
Adsorbent
28/12 Ball Joint
Glass Fritted Disc
Glass Wool Plug
Glass Water Jacket
Fritted Stainless Steel Disc
16mm Solv-seal Joint

Figure 2-3. Acceptable sorbent module design #2.

pressure) shall be requested and an adjustment for elevation difference between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.11 Crushed Ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient air temperatures.

2.1.12 Glass Wool. Used to plug the unfritted end of the sorbent module. The glass wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hours and air-dried prior to use.

2.1.13 Gas Density Determination Equipment. The fixed gas samples for determining the stack gas density during the sampling run are taken using an integrated gas sampling train. The gas sample is bled through a nonreactive probe and an air-cooled condenser or equivalent which removes excess moisture from the gas stream and cools the hot gas to ambient temperatures. The sampling flowrate is measured with a flow rate meter and controlled by a needle valve. The sample is collected in a leak-free bag and analyzed with an ORSAT appraratus. Detailed specifications may be found in EPA Method 3.[2]

2.1.14 Calibration/Field Preparation Record. For documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2®, quality assurance/quality control check results, dry gas meter and thermocouple calibrations, etc.), a permanently-bound laboratory notebook is required, in which duplicate copies of the data may be made as they are being recorded. The duplicate copies should be detachable and stored separately in the test program archives.

2.2 Sample Collection Media

2.2.1 Filters. Glass or quartz fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) for 0.3 um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71.[4] Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of type that is unreactive to these acid gases.[3] Reeve Angel® 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

2.2.2 Adsorbent Resin. Porous polymeric resin, XAD-2®, shall be used. The resin must be cleaned prior to use, according to the procedure outlined in Appendix B of this method. Once cleaned, the resin should be stored in an air-tight wide-mouth amber glass container with a Teflon®-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon® film and elastic bands. The resin should be used within four weeks of the preparation. Additional details are found in Section 3.

2.2.3 Silica Gel. Indicating type, 6 to 16 mesh. Dry at 175°C (350°F) for 2 hours before using.

2.2.4 Impinger Solutions. Distilled organic-free water shall be used to charge the impingers. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger: the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated, as sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate and possibly plug the impinger. Additional details are found in Section 3.

2.3 Materials and Supplies Needed for Sample Recovery

2.3.1 Methanol/Methylene Chloride. Methanol and methylene chloride are used for sample recovery and clean-up. Screening details are given in Section 3.

2.3.2 Water. Organic-free water shall be used to aid in quantitatively transferring any impinger solutions that will be analyzed.

2.3.3 Probe Liner, Nozzle and Organic Module Brushes. Nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon®, or inert material equal to the length of the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the nozzle and the organic module conditioning section.

2.3.4 Wash Bottles. Teflon® or glass wash bottles are required; polyethylene wash bottles should not be used as organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

2.3.5 Glass Sample Storage Containers. Chemically resistant, borosilicate amber and clear glass bottles, 500 mL and 1,000 mL. Screw cap liners shall either be Teflon® or otherwise constructed to be leak free and resistant to chemical attack by organic recovery solvents.

2.3.6 Petri Dishes. Glass, sealed around the circumference with wide (1 in) Teflon® tape, for storage and transport of filter samples.

2.3.7 Graduated Cylinder and/or Triple-Beam Balance. To measure condensate water to the nearest 1 mL or 1 gram. Graduated cylinders shall have subdivisions no greater than 2 mL. Laboratory triple-beam balances capable of weighing to ±0.5 gram are required.

2.3.8 Nalgene® Storage Containers. Screw cap polypropylene or polyethylene containers to store silica gel.

2.3.9 Funnels. Glass funnels are required to aid in the recovery of samples for organic analyses.

2.4 Sample Preparation and Analysis

2.4.1 Gas Chromatograph/Mass Spectrometer (GC/MS). A GC/MS coupled to a computer for data acquisition is required for compound identification and quantification. The GC portion of the instrument should be equipped with a fused silica capillary column and be capable of temperature programming. The mode of sample injection should be on-column, but split/splitless injection is acceptable if the split ratio is accurately known giving adequate detectability. Details of the analytical column and analytical parameters are given in Section 4.4.

The MS portion should have at least the following capabilities:

- electron ionization (EI), 70 ev (nominal);
- scanning 35-450 mass units/second;
- single (or selected) ion monitoring; and
- a minimum detectable limit of approximately 25 ng per component on column.

2.4.2 Glassware. All glassware is to be cleaned before use by the procedure given in Appendix A. A "glassware" blank is required for the Soxhlet extractor, empty glass thimble, and concentration apparatus. The blank is prepared by charging the extractor with 300 mL of the sample extraction solvent, cycling the extractor overnight, concentrating the solvent to 1 mL and analyzing by GC/MS as described in Section 4.4. This 1 mL sample should be screened for the compounds of interest. (This assay could also serve as the required screening of the extraction solvent as discussed in Section 3.2.2.) Each Soxhlet set-up should be distinctly marked and should have a corresponding sample concentrator identically marked. These two apparatuses should always be used in pairs to facilitate the identification of any contamination problems. If the glassware blank indicates contamination, a solvent rinse of the entire system should be performed, charged with solvent and again cycled overnight as described above. Continue this process until the blank is free of the components of interest at the minimal detection limit (MDL) of the GC/MS. If contamination persists at the same level, the solvent purity should be investigated.

2.4.2.1 Soxhlet Extractor. Consisting of a 500 mL receiver extractor, condenser, and glass thimble with an extra coarse ground glass-frit.

2.4.2.2 Kuderna-Danish Evaporative Concentrator (K-D). 500 mL size with a 15 mL graduated receiver and a Snyder column. Micro K-D's for reducing sample down to 1 mL.

2.4.2.3 Sample Vials. 2 mL and 10 mL size. Vials should be equipped with Teflon®-lined screw caps.

2.4.2.4 Volumetric Flasks. 10-100 mL size. Used for preparing standards.

2.4.2.5 Funnels. Used for transferring solvent to K-D and containing the desiccant, Na_2SO_4.

2.4.2.6 Glass Wool. Cleaned by Soxhlet extraction for 12 hours with extraction solvent. Used as support for bed of Na_2SO_4 desiccant and to prevent the XAD-2® from floating from the thimble during extraction.

2.4.2.7 Miscellaneous Beakers. 10-400 mL size.

2.4.2.8 Disposable Pipets. For transferring sample to vials.

2.4.2.9 Separatory Funnels. 250 and 500 mL size with Teflon® stopcock.

2.4.2.10 Graduated Cylinders. 100 and 500 mL size.

2.4.3 Syringes. 10 and 100 µL size. Use separate syringes for injecting sample into the GC/MS and spiking surrogate compounds.

2.4.4 Drying Oven. Vacuum or convection type. 0-300°C.

2.4.5 Analytical Balance. Capable of weighing to the nearest 0.1 mg.

2.4.6 Stainless Steel Tongs. For transferring thimble to extractor.

2.4.7 Boiling Chips. Teflon® boiling chips, cleaned in batch quantities by Soxhlet extraction for 12 hours using the sample extraction solvent.

3. Reagents

It is imperative that all reagents be screened for organic pollutants (i.e., compounds of interest or compounds that may interfere with the analysis) by GC/MS before use in either sampling or analytical procedures. Once a particular "lot" has been deemed acceptable by the established criteria, the same lot must be used to complete all analyses.

3.1 Solvents. The solvents used for both the sampling and analysis must be screened prior to use regardless of the indicated purity. Solvents can be purchased and screened by "lot number" thus eliminating the necessity to screen each bottle. Solvents classified as "Distilled in Glass", "Pesticide Grade", "GC/MS Grade", etc. are generally free of most impurities.

Organic solvents are screened by concentrating 500 mL of the solvent to 1 mL and analyzing by GC/MS as described in Section 4.4. The presence of any compound of interest at a level greater than 5 µg/mL (5 ng/µL) in the concentrate will be cause for the rejection of the particular lot number.

Organic-free water is screened by solvent extraction, utilizing a separatory funnel. A 200 mL aliquot is extracted three times with 50 mL portions of pre-screened methylene chloride. The extract is concentrated to 1 mL and analyzed by GC/MS. The presence of any compound of interest at a level greater than 5 µg/mL will be cause for the rejection of the particular lot number.

3.2 Sodium Sulfate (Na_2SO_4). Sodium sulfate is used to remove any traces of water from the solvents before concentration. Reagent grade Na_2SO_4 is cleaned by multiple washings (5-6) with the sample extraction solvent. The cleaned Na_2SO_4 is dried in an oven (vacuum, preferably; convection, alternatively) at 105°C.

3.3 Deionized Organic-Free Water. Water suitable for washing glassware is prepared by first treating with ion-exchange resins followed by charcoal filtration. Water prepared in this manner should exhibit a resistivity in excess of 18 meg-ohms. The organics level is greatly reduced over tap water but the "organic-free" water is generally not free of trace levels of organics. Organic-free water is also commercially available.

3.4 XAD-2® Resin. XAD-2® (20/60 mesh) can be obtained from any of several vendors of chromatography supplies and accessories either precleaned or as supplied by the manufacturer. (Precleaned resin is defined by the procedure given in EPA 600/7-78-201, Appendix B.) Precleaned resin should be screened before use by subjecting a 20 g portion to solvent extraction and analysis procedures. New XAD-2® should be cleaned by the procedure outlined in Appendix B of this method with the final extraction solvent being concentrated and screened for impurities by GC/MS. If the cleanliness criteria are not met, repeat the final extraction step until the criteria are met. If the resin is not deemed "clean" by the third repeat, check for sources of contamination such as glassware and/or solvent. The glassware and solvents can be screened for contaminants by performing an extraction/analysis sequence without the presence of XAD-2®. The final extraction solvent is defined as the solvent to be used to extract the sample components from the XAD-2® after sampling. The resin may be extracted in small batches, individually screened, and then combined (if desired) or extracted in bulk. The cleaned resin can be stored in clean amber jars at room temperature (25°C) or less in an area that has minimal levels of possible contaminants (i.e., do not store in a refrigerated area used to contain samples and/or standards). Alternatively, the resin can be packed in the glass sampling modules and capped. Sampling should be scheduled as soon as possible after resin clean-up has been completed. The shelf life has been determined to be about four weeks. The XAD-2® sampling modules should be shipped to and from the laboratory on ice.

3.5 Standards. Standards, as the neat compound, should be obtained in the purest form available, usually "99+ percent purity." These compounds should also be obtained in the stable isotopic labeled form, if possible, for use as surrogate spikes.

3.6 Nitrogen. High purity nitrogen (see Appendix B) in compressed gas cylinders is required for sample concentration and the removal of solvent from the XAD-2® resin after clean-up.

3.7 Helium. High purity helium (<0.5 ppm total hydrocarbon) in compressed gas cylinders is used as carrier gas for the GC/MS.

4. Procedure

4.1 Sampling.

4.1.1 Pretest Preparation. The complexity of this method is such that, in order to obtain reliable results, field personnel shall be trained in the use of the test procedures. All the components shall be maintained and calibrated according to the procedure described by Rom[6] unless otherwise specified.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Filters should be preweighed if particulate loading is to be determined. Label the shipping containers (glass petri dishes) and keep the filters in these containers at all times except during sampling.

4.1.2 Preliminary Determination. Select the sampling site and the minimum number of sampling points according to EPA Method 1.[2] Determine the stack pressure, temperature, and the range of velocity heads using EPA Method 2.[2] It is recommended that a leak-check of the pitot lines (EPA Method 2,[2] Section 3.1) be performed. Determine the stack gas moisture content using the EPA Approximation Method 4[2] or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2,[2] Section 3.6. If the integrated EPA Method 3[2] sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of preliminary gas stream velocity measurements so that it is not necessary to change the nozzle in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocities encountered; see Section 2.2 of EPA Method 2.[2]

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the probe.

Typically three (3) dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHC's from incineration systems.[10] Additional sample volume shall be collected as necessitated by analytical detection limit constraints. Consideration should also be given to specific retention volume data on a compound by compound basis. If such data are not available, the information must be established for the compound(s) of interest to avoid inaccurate results.

Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate to the volume requirement. Allocate the same time to each traverse point defined by EPA Method 1.[2] The length of time sampled at each traverse point should be an integer or an integer plus one half minute to avoid timekeeping errors.

In some circumstances, (e.g., incinerator waste being fed in batches) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes.

4.1.3 Preparation of the Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is initiated.

The XAD-2® sorbent traps are prepared in the laboratory by filling with 20 grams of clean resin. While filling, distribute the resin uniformly to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, causing the resin to cling to the trap walls. This may be minimized by filling the trap in the presence of an ionizing source such as Polonium-210 which acts as an antistat to remove the static charge carried by the resin. Commercial antistatic devices are the Model-204®* and Model-210®*, available from the 3-M Company, Inc., St. Paul, MN.

Place 100 mL of distilled-deionized organic-free water in each of the first two impingers following the knockout trap, leave the third impinger empty (or charge with caustic solution as necessary), and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the silica gel plus impinger may be weighed together to the nearest 0.5 g and the weight recorded.

Using tweezers or clean disposable surgical gloves, place a labeled (identified) filter in the filter holder. Be sure that the filter is properly centered and the gasket placed to prevent the sample gas stream from bypassing the filter. Visually check the filter for tears or lifting after assembly is complete.

When glass liners are used, install the selected nozzle using a Viton-A O-ring if stack temperatures are less than 260°C (500°F) and a woven glass fiber gasket when temperatures are higher. See Rom[6] for details. Other connecting systems using either 316 stainless steel or Teflon® ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection.

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*Registered trademarks of the 3-M Company, Inc., St. Paul, MN.

Set up the train as in Figure 2-1. If necessary, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to contain large particles or when water droplets are present in the stack.

Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

Place crushed ice around the impingers and the organic module condensate knockout.

Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Insure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2® resin temperature never exceed 50°C (122°F), as thermal decomposition will occur. During testing, the XAD-2® temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. Since the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pretest leak-check is required.

A lower vacuum may be used, provided that it is not exceeded during the test. Leak test by first attaching to the inlet of the filter holder (cyclone, if applicable) a carbon-filled leak check impinger shown in Figure 4-1, plugging the inlet and evacuating to 381 mm Hg (15 in Hg). Once the train has passed the leak check criteria, the probe should be connected to the train, the end plugged, and the train leak-checked at 25 mm Hg (1 in Hg). Alternatively, the probe may be leak-checked simultaneously with the rest of the sampling train, in one step, at 381 mm Hg (15 in Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, is unacceptable and must be corrected.

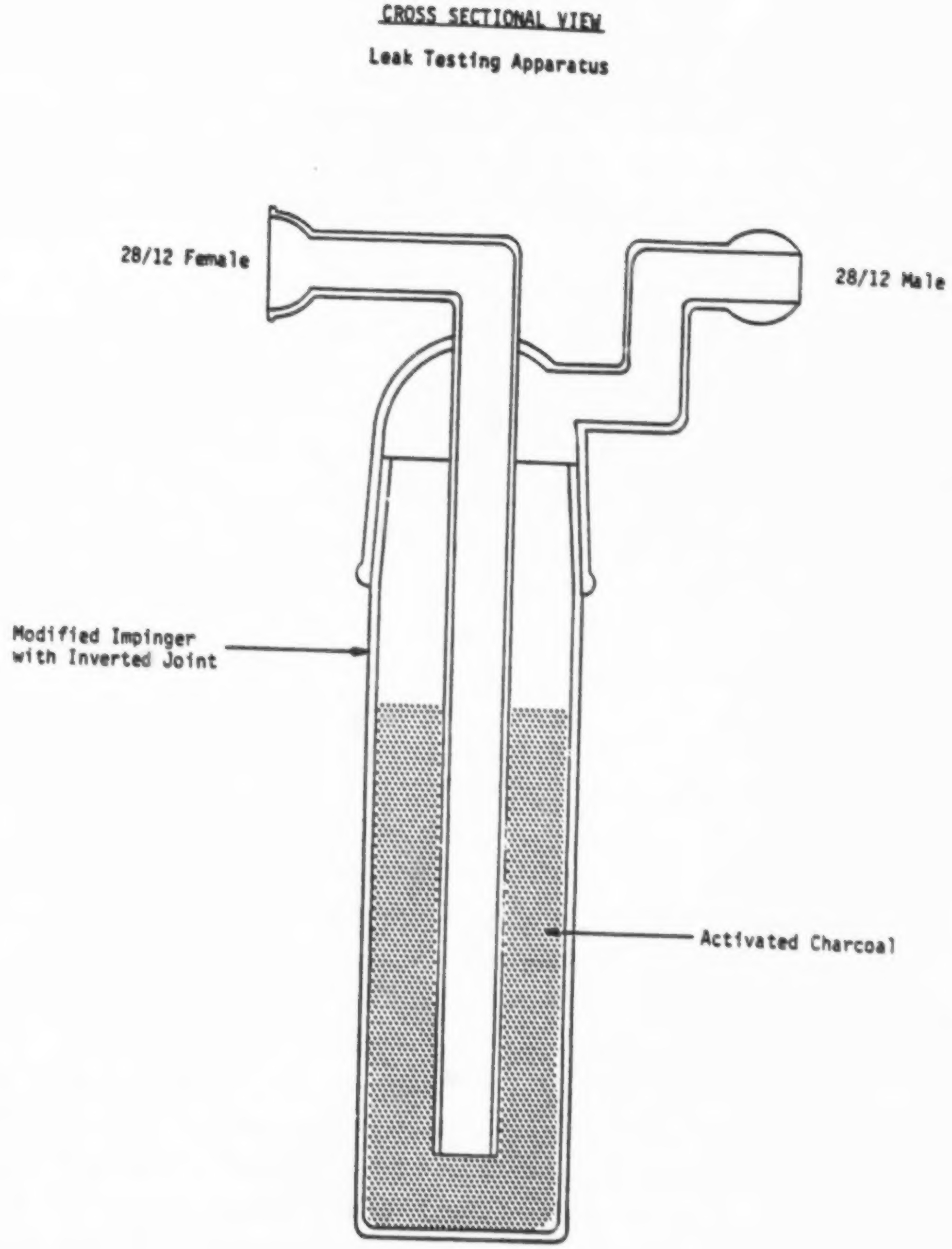

CROSS SECTIONAL VIEW
Leak Testing Apparatus
28/12 Female
28/12 Male
Modified Impinger with Inverted Joint
Activated Charcoal

Figure 4-1. Leak check impinger.

These specific leak-testing instructions described in Rom[6] are strongly recommended. Start the pump with fine adjust valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the fine adjust valve until the desired vacuum is reached. Do not reverse direction of the fine adjust valve; this will cause water to back up into the organic module or between the impingers. If the desired vacuum is exceeded, leak-check as instructed below and begin again.

When the leak-check is completed, slowly remove the plug from the inlet to the leak check apparatus. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse adjust valve. Switch off the pumping system and reopen the fine adjust valve. Do not reopen the fine adjust valve until the coarse adjust valve has been closed to prevent the water in the impingers from being forced backward or the organic module and the silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sampling Run. If during the sampling run, a component (e.g., filter assembly, impinger or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 except that it shall be done at a vacuum equal to or greater than the maximum value recorded at that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall void the run unless it is impossible to repeat, in which case he/she shall record the leakage rate and plan to correct the sample volume as shown in Section 6.2 of this method. It should be noted that correction of the sample volume in this manner reduces the integrity of the pollutant concentrations data generated and must be avoided.

Immediately after a component change, and before sampling is re-initiated, a leak-check similar to a pretest leak-check must also be conducted.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. Use the procedure outlined above insuring that the leak-check is conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. If the leakage rate is found to be not greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall attempt to repeat the run as previously discussed. If the run cannot be repeated, the tester shall record the leakage rate, correct the volume as shown in Section 6.2 of this method and shall consider the data obtained of questionable reliability.

4.1.5 Sample Collection. During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic. Maintain a temperature around the filter of 120 ± 14°C (248 ± 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

For each run, record the data required on a data sheet. Take care to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take readings at least once at each sampling point during each time increment. Level and zero the manometer initially and periodically throughout the sampling run.

Clean the stack access ports prior to the test run to eliminate the possibility of sampling deposited material. To begin sampling, remove the nozzle covering, verify that the filter and probe heating systems are at the specified temperature, and that the pitot tube and probe are properly positioned. Place the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. Rom[6] details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the stated ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.[7]

When the stack is under significant negative pressure (equivalent to the height of impinger stem) take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the organic module. It may be necessary to turn the pump on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and stack accesss port to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by EPA Method 1.[2] Take care not to bump the probe nozzle into the stack walls when sampling near the walls or when removing and inserting the probe through the access port.

During the test run, make periodic adjustments to keep the temperature of the filter holder and the organic module at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the condenser outlet.

If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling rates difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. It is recommended that another complete filter holder/sorbent trap assembly be used rather than attempting to change the filter and resin themselves. After a new filter holder/sorbent trap assembly is installed, conduct a leak-check.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or in cases where equipment failure necessitates a change of trains.

> Note: When two or more trains are used, separate analysis of the front-half (if applicable) organic module and impinger (if applicable) catches from each train may be performed, unless identical nozzle sizes were used on all trains. Then the front-half catches from the individual trains may be combined (as may the impinger

catches) and one analysis of front-half catch and one analysis of impinger catch may be performed.

At the end of the sample run turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Leak-check the pitot lines as described in EPA Method 2,[2] Section 3.1. The lines must pass this leak-check in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinecity. Calculate percent isokineticity (see Calculations, Section 6) to determine whether the results are acceptable or whether another test run should be made.

4.2 Sample Recovery.

4.2.1 Disassembly of the Semi-VOST Train. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

4.2.1.1 When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling, as this will create a vacuum in the filter holder drawing water from the impingers back into the sorbent module.

Before moving the sampling train to the cleanup site, remove the probe from the sample train and cap the open outlet, taking care not to lose any condensate that might be present. Cap the filter inlet. Remove the umbilical cord from the last impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

4.2.1.2 Cap the filter holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas conditioning section. Cap all organic module openings. Disconnect the organic module knockout trap from the impinger train inlet and cap both of these openings. Ground glass stoppers, Teflon® caps or caps of other inert materials may be used to seal all openings.

4.2.1.3 Transfer the probe, the filter, the organic module components and the impinger assembly to the clean-up area. This area should be clean and protected from the elements to minimize sample contamination or loss.

4.2.1.4 Save a portion of all washing solutions (methanol/methylene chloride, distilled-deionized water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle used and place them in separate labeled glass sample containers.

4.2.1.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

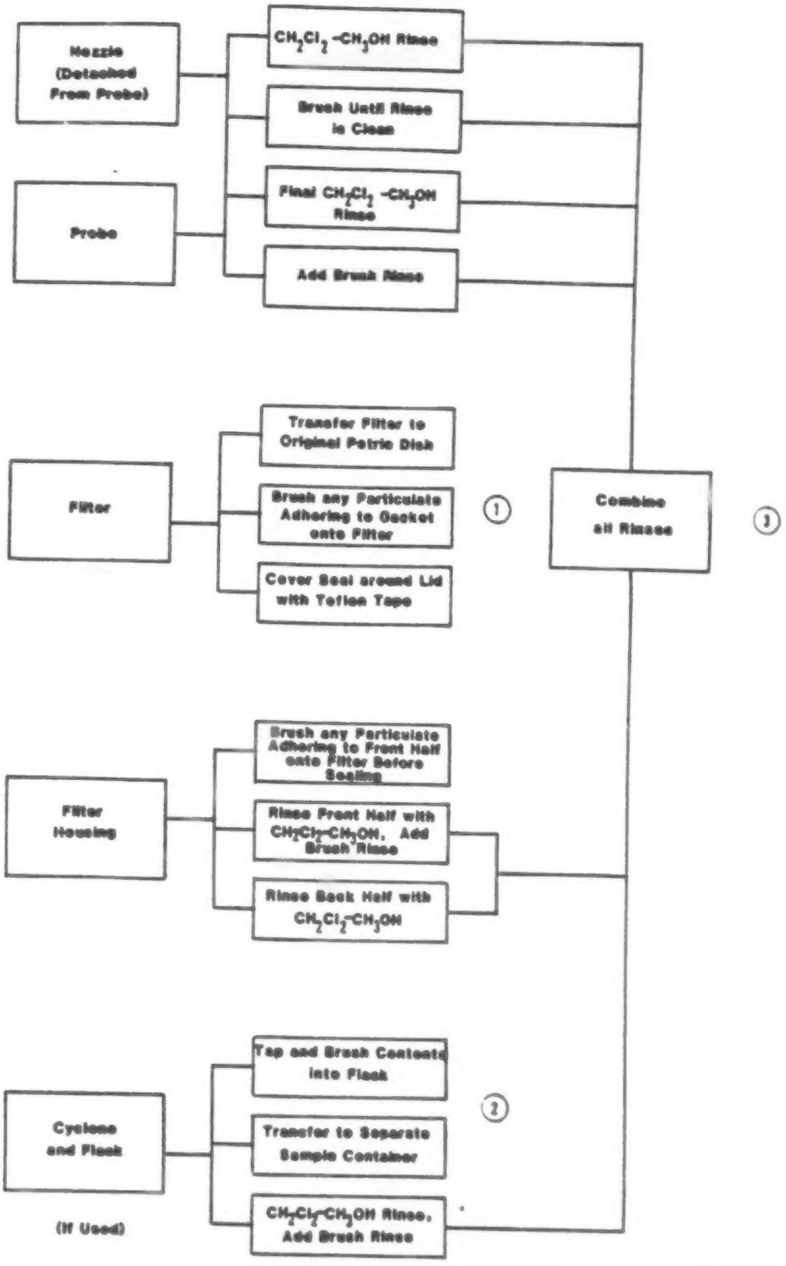
4.2.2 Sample Handling and Transfer. Step-by-step sample handling and transfer procedures are outlined below. Flow diagrams for these recovery procedures are presented in Figures 4-2, 4-3, and 4-4. An example coding format for Semi-VOST samples follows in Table 4-1.

4.2.3 Probe, Nozzle, Cyclone (if used), Filter Recovery.

4.2.3.1 Carefully remove the filter from the filter holder and place it in its identified petri dish. Use two pairs of tweezers to handle the filter. If it is necessary to fold the filter, insure that the particulate cake is inside the fold. Carefully transfer to the petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, using a dry nylon bristle brush and/or a sharp-edged blade. Label the container and seal with wide (1 in) Teflon® tape around the circumference of the lid.

4.2.3.2 Taking care to see that dust on the outside of the probe or other exterior surfaces does not contaminate the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe liner, and front half of the filter holder by washing these components first with 50 to 75 mL of methanol and then an equal volume of methylene chloride into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as the samples. Perform rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particulate material. Then make a final rinse of the inside surface with the solvent mix.


Nozzle (Detached From Probe)
Probe
CH_2Cl_2 -CH_3OH Rinse
Brush Until Rinse is Clean
Final CH_2Cl_2 -CH_3OH Rinse
Add Brush Rinse
Filter
Transfer Filter to Original Petrie Dish
Brush any Particulate Adhering to Gasket onto Filter
Cover Seal around Lid with Teflon Tape
①
Combine all Rinses
③
Filter Housing
Brush any Particulate Adhering to Front Half onto Filter Before Sealing
Rinse Front Half with CH_2Cl_2-CH_3OH, Add Brush Rinse
Rinse Back Half with CH_2Cl_2-CH_3OH
Cyclone and Flask
(If Used)
Tap and Brush Contents into Flask
Transfer to Separate Sample Container
②
CH_2Cl_2-CH_3OH Rinse, Add Brush Rinse

Notes: All Containers for Samples for Organic Analysis must be Glass. Use Teflon or Glass Wash Bottles. Teflon is Preferred.

Figure 4-2. Semi-VOST train sample handling and transfer: nozzle, probe, cyclone (if used) and filter.

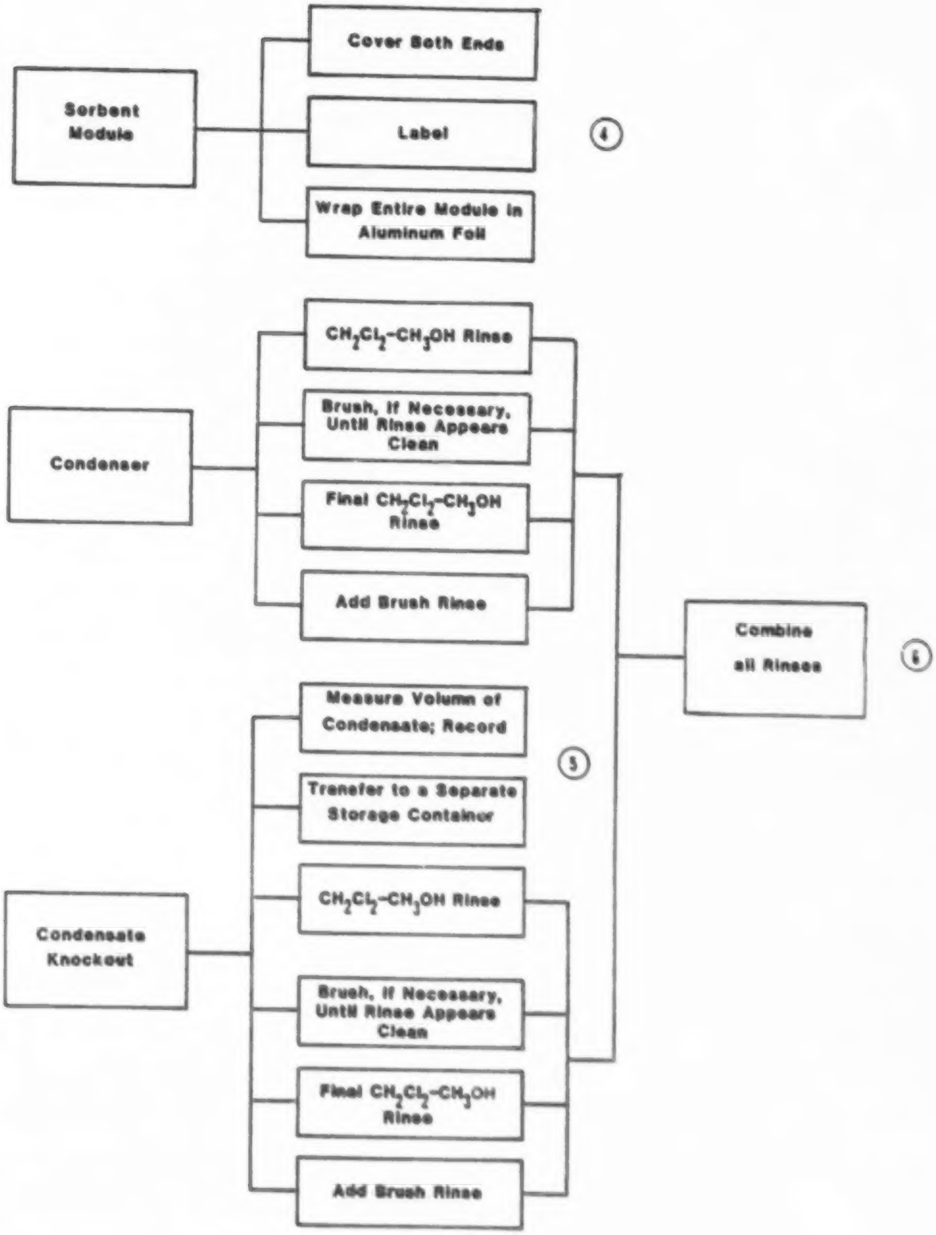

Sorbent Module
Cover Both Ends
Label
Wrap Entire Module in Aluminum Foil
④
Condenser
CH_2Cl_2-CH_3OH Rinse
Brush, If Necessary, Until Rinse Appears Clean
Final CH_2Cl_2-CH_3OH Rinse
Add Brush Rinse
Combine all Rinses
⑥
Condensate Knockout
Measure Volume of Condensate; Record
Transfer to a Separate Storage Container
⑤
CH_2Cl_2-CH_3OH Rinse
Brush, If Necessary, Until Rinse Appears Clean
Final CH_2Cl_2-CH_3OH Rinse
Add Brush Rinse

Figure 4-3. Semi-VOST train sample handling and transfer: organic module section.

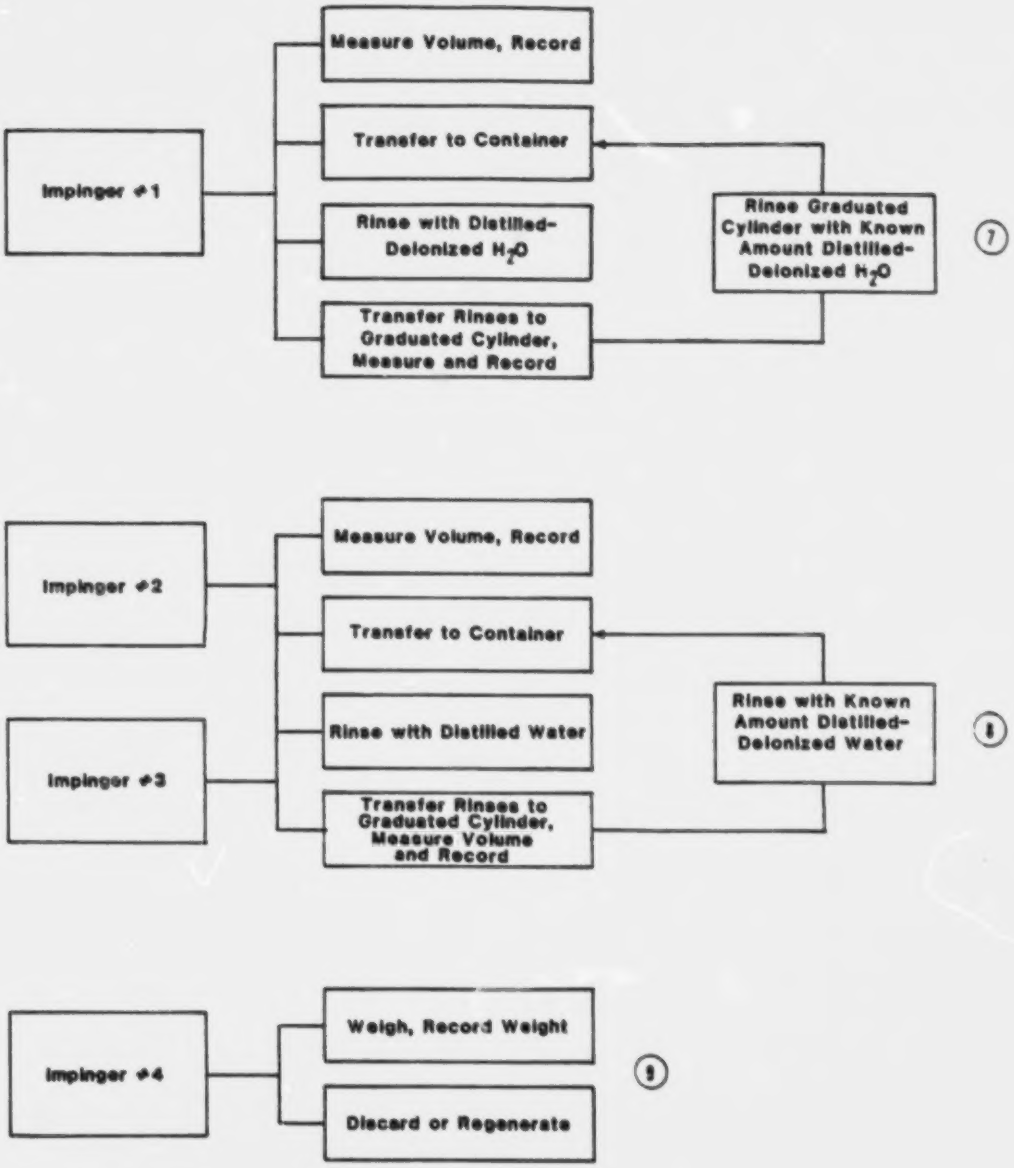

Impinger #1
Measure Volume, Record
Transfer to Container
Rinse with Distilled-Deionized H_2O
Transfer Rinses to Graduated Cylinder, Measure and Record
Rinse Graduated Cylinder with Known Amount Distilled-Deionized H_2O
⑦
Impinger #2
Impinger #3
Measure Volume, Record
Transfer to Container
Rinse with Distilled Water
Transfer Rinses to Graduated Cylinder, Measure Volume and Record
Rinse with Known Amount Distilled-Deionized Water
⑧
Impinger #4
Weigh, Record Weight
Discard or Regenerate
⑨

Figure 4-4. Semi-VOST train sample handling and transfer: impinger train.

Table 4-1. EXAMPLE CODING FORMAT FOR SEMI-VOST TRAIN SAMPLES

Sample code	Order of recovery[a]	Container	Size	Sample preparation[b]	Sample description
PF	1	Glass petri dish(es)	150 mm diameter	4.3.4	Particulate filter(s)
CC	2	Amber glass	100 mL, widemouth	4.3.4	Cyclone catch (if applicable)
FHR	3	Clear glass[c]	1 L	4.3.5	Front-half rinse (50:50 methanol/methylene chloride) i.e., nozzle, probe, filter housing, cyclone
SRB		Clear glass[c]	500 mL	4.3.5	Solvent rinse blank (50:50 methanol/methylene chloride)
XAD	4	Sampling module	100 mL, widemouth or capped sorbent traps	4.3.3	XAD-2® resin sample(s)
CD	5	Amber glass	1 L	4.3.1	Condensate knockout catch
BHR	6	Clear glass[c]	1 L	4.3.5	Back-half rinse (50:50 methanol/methylene chloride) i.e., condenser and knockout traps

(continued)

Table 4-1. Concluded

Sample code	Order of recovery[a]	Container	Size	Sample preparation[b]	Sample description
I-1	7	Amber glass	1 L	4.3.2	First impinger catch and rinse
I-1B		Amber glass	1 L	4.3.2	First impinger blank (appropriate collecting solution)
I-2,3	8	Amber glass	1 L	4.3.2	Second and third impinger catches combined and rinsed
I-2,3B		Amber glass	1 L	4.3.2	Second and third impinger blank (appropriate collecting solution)
I-4	9	Clear glass	1 L	4.2.5	Silica gel

[a] See Figures 4-2, 4-3, and 4-4.

[b] See appropriate sections of the Semi-VOST method.

[c] Must be clear to allow tester to verify when components have been "rinsed clean"; cover with aluminum foil to protect sample from light.

Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A funnel (glass) may be used to aid in transferring liquid washes to the container. Follow the solvent rinse with a brushing. Both persons should support the probe in an inclined position, while one sprays solvent into the upper end of the liner as the other pushes the probe brush with a twisting action through the probe; the second person must place a sample container underneath the lower end of the probe, and catch any solvent and particulate matter which is brushed from the probe. Run the brush through the probe three or more times until no visible particulate material is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, it is necessary to run the brush through in this manner at least six times since these probes have small crevices in which particulate matter can be entrapped. Rinse the brush with solvent, and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe. Between sampling runs, keep brushes clean and protected from contamination.

4.2.3.3 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (50:50) mixture. Rinse each surface at least three times to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if used). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected, tighten the sample container lid so that solvent will not leak out upon shipment to the laboratory. Mark the height of the fluid level to allow determination of whether or not leakage occurred during transport. Label the container clearly to identify its contents.

4.2.4 Condenser, Sorbent Module and Condensate Knockout Recovery.

4.2.4.1 The sorbent trap section of the organic module is used as a sample transport container. Ground glass stoppers or Teflon® caps are used to seal the ends. The sorbent trap should then be labeled, covered with aluminum foil and transported to the laboratory on ice.

4.2.4.2 Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL using a graduated cylinder or by weighing to within ±0.5 g using a triple-beam balance. Record the volume or weight of liquid present, and note any discoloration or film in the liquid catch. Transfer this liquid to a labeled glass container. Inspect the backhalf of the filter housing, and the gas conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume as described above. Add this material to the condensate knockout trap catch.

4.2.4.3 All sampling train components located between the high efficiency glass or quartz fiber filter and the first wet impinger (including the heated Teflon® line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (50:50) mixture, and the rinsings combined. The rinsings shall be separated from the condensate. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to the appropriate sample.

4.2.5 Silica Gel and Impingers Recovery.

4.2.5.1 Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may facilitate pouring the silica gel without losses. A rubber policeman may be used to aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids in the transfer. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

4.2.5.2 Recover the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ±0.5 g by using a triple-beam balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Amber glass containers are used for storage of the impinger catches.

4.2.6 Sample Preparation for Shipment. Prior to shipment recheck all sample containers to insure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon® tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

4.3 Sample Preparation for Analysis. The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1-10 mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated napthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

4.3.1 Condensate. The "condensate" is the moisture collected in the first impinger following the XAD-2® module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10 mL aliquots of the extraction solvent and added to the separatory funnel.

The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for five minutes. After complete separation of the phases, remove the solvent and transfer to a K-D, filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 Nsodium hydroxide and re-extract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon® boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS) the sample is ready for analysis as discussed in Section 4.4.

4.3.2 Impinger Contents. Spike the sample with the surrogate standards, measure and record the volume and transfer to a separatory funnel. Proceed as described in Section 4.3.1.

4.3.3 XAD-2®. Spike the resin directly with the surrogate standards. Transfer the resin to the all glass thimbles by the following procedure. (Care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices.) Suspend the XAD-2® module directly over the thimble. The glass frit of the module (see Figure 2-2) should be in the up position. The thimble is contained in a clean beaker which will serve to catch the solvent rinses. Using a Teflon® squeeze bottle, flush the XAD-2® into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2® glass wool plug to the thimble. Cover the XAD-2® in the thimble with a precleaned glass wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction without a spike is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon® boiling chips and assemble the apparatus. Begin the extraction immediately after completing the assembly of the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hour. Extract the resin for 16 hours. Separate out any water present in the extract and add it to the condensate. If water soluble compounds are being analyzed and if it has been shown that the compounds are not extracted efficiently with methylene chloride, extract the XAD-2® resin a second time with methanol. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Section 4.3.1.

4.3.4 Particulate Filter (and cyclone catch). If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2® resin.

4.3.5 Train Solvent Rinses. All train rinses, (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container the intended spike is divided equally among the containers proportioned from a single syringe volume.

Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Section 4.3.1.

4.4 Sample Analysis. The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused silica capillary GC columns. Because of the nature of GC/MS instrumentation and the cost associated with sample analysis, pre-screening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture GC/ECD is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keeping in mind that GC/FID has a slightly lower detection limit than GC/MS, the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

The mass spectrometer will be operated in a full scan (40 to 450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Appendix C of this document, for each of the designated POHCs in an incinerator effluent analysis.

For most purposes, electron ionization (EI) spectra will be collected since a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification.

4.4.1 GC Conditions. The GC should be equipped with fused silica capillary columns for compound separation. Fused silica columns provide the compound separation often necessary for accurate quantitation of a complex sample. Additionally, the inertness of the column itself greatly improves the versatility for samples that contain both polar and non-polar compounds. The conditions for the GC are given below.

- Column: 30 m x 0.32 mm ID fused silica capillary (1 μ film thickness), coated with SE-54 or equivalent.
- Injector Temperature: 280°C.
- Column Temperature: 40°C for 4 minutes then 40-270°C @ 10°/minute. Hold at 270°C until no evidence of eluting peaks.
- Carrier Gas: High purity He flowing @ 1 mL/minute.
- Injection Volume: 1 μL.
- Electron Energy: 70 eV (nominal).

The injection system can be either on-column or split/splitless. The column performance should be checked at least weekly by injecting a test mixture (such as a Grob mix) commercially available from suppliers of chromatography accessories.

The temperature program may be changed if required to accomplish a difficult separation.

4.4.2 MS Conditions. In general, the cycle time between collections of complete mass spectra needs to be selected to be compatible with elution of the components in the sample. For capillary column GC separations, the cycle time will be on the order of one second. Longer cycle times may lead to distortion of the spectra. To adequately characterize a GC peak, at least five spectra will be collected across the peak. For low level components in the extract, the elution peak may be less than 3 seconds wide and it might not be possible to collect enough scans to characterize the GC peak, if the scan repetition rate were greater than 1 second.

To insure consistency with sources of mass spectra, the GC instrumentation will be tuned to meet the spectral criteria for decafluorotriphenylphosphine. The criteria for meeting the tuning requirements are found in EPA Federal Register Method 625 and summarized in Table 4-2.

Typical MS conditions are given as follows.

- Scan Range: 40 to 450 amu.
- Scan Rate: 1 scan/second.

4.4.2.1 Qualitative Identification. The identification of organic POHCs is based both on the chromatographic elution of those compounds and on the specificity of the detection system. The relative retention time of a POHC compared to an appropriate internal standard is generally constant to within about ±0.2 percent, depending upon the compound. For GC/MS, a match in both the relative retention time for the POHCs and the simultaneous elution of multiple analytical ions specific to that POHC will serve to establish the qualitative identification of the components of the sample.

For directed analyses, where specific POHCs are to be measured in the sample, the identification criteria to confirm the presence of a POHC by MS are that the GC retention time for the suspect peak relative to some standard match that for the corresponding POHC and that the characteristic ions of the suspected POHC are present in the unknown

Table 4-2. TUNE CRITERIA FOR DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Mass	Ion abundance criteria[a]
51	30 to 60
68	<2% of mass 69
70	<2% of mass 69
127	40 to 60
197	<1
198	100 (base peak)
199	5 to 9
275	10 to 30
365	>1
441	Present, but less than mass 443
442	>40
443	17% to 23% of mass 442

[a] All values in percent abundance relative to mass 198, unless otherwise stated.

sample at approximately the same ratio as is present in the standard and that those ions coelute. For those POHCs which may be analyzed with MS detection, Appendix C lists the characteristic ions for use with either electron or chemical ionization.

A key factor in the use of computerized mass spectral search systems is the data base. Ideally, the data base would include spectra of all of the potential compounds of interest and would have been obtained under the same conditions for the GC and the MS as for the incinerator process samples. As a practical alternative, the NBS data base will be used and supplemented with spectra for those POHC compounds which are not in the library, preferably obtained on the instrument to be used for the sample analysis.

A second key factor in the use of computerized mass spectral search systems is the assessment of the confidence to be placed in a qualitative compound identification or "match" with the reference spectrum in the library. The computerized search system typically generates one or more numerical indicators of the "goodness of fit." In the Finnigan INCOS data system, for example, goodness of fit is indicated by three values:

- the fit - how well each library entry is represented in the sample spectrum;
- the reverse fit - how well the sample spectrum is represented in each library entry; and
- the purity - how well both the fit and the reverse fit match the sample spectrum and the library entry.

Of these terms, the purity is the most powerful since a high purity value indicates that both the library entry and the sample spectrum match each other closely and either spectrum accounts for virtually all of the other spectrum. When using a Finnigan INCOS GC/MS/DS, it would be appropriate to base qualitative compound identifications of POHCs on the purity value. For purity values in excess of 900 on the 0 to 1,000 scale, the computer search could be regarded as having identified a single component in the GC peak. A list of the top 5 to 9 choices can also be retrieved as output from the search system. If several compounds are identified with purity values that are close to one another, the analyst should retrieve and examine the library spectra and use the elution order data to ascertain the best candidate for the identity of the GC peak of interest. Similarly, if the purity value has decreased below the 900 value threshold, the analyst should retrieve and examine the library spectra, the sample spectrum, and any retention time data to identify the sampling compound.

The algorithms for calculating "goodness of fit" parameters and the numerical values that are associated with specific levels of confidence in the identification will vary depending on the particular software in the GC/MS system employed for analysis. For this reason, and also because the professional judgment of the mass spectrometrist is an essential element in the qualitative compound identification process, it is not appropriate to specify in this document numerical goodness of fit criteria to be applied to all POHC analyses.

It is essential, however, that all compound identifications be reported with an indication of the goodness of fit criteria that were used in making the assignment. These may include numerical values of parameters from the computerized search system and/or the analyst's professional judgment (e.g., "strong", "probable", "tentative"). Of course, elution order retention time and accordance with the reference spectrum must be utilized to assure correct identification of any and all POHCs in samples from the emissions of hazardous waste incinerators.

4.4.2.2 Quantitation. Prior to analysis, each sample is spiked with a known amount of the internal standard. The response ratio (or factor) of the internal standard (phenanthrene-d_{10}) to the compounds of interest in the sample is then compared to a similar ratio established utilizing an instrument calibration.

The response factor calibration for the individual compounds is established by using a five-point calibration curve with nominal compound levels of 10, 25, 100, 250, and 500 µg/mL. This calibration is established using the compounds of interest at concentrations that will bracket the working range of the anticipated sample concentrations. Sample concentrations can be modified either up or down to fit this range. The quantitation standard will be spiked into the samples so the concentration will fall within the calibration curve.

Calibration methods, using either the raw response of a standard or the relative response of the analyte versus an internal standard as a function of the amount of analyte, are widely used in analytical chemistry for quantification. For these methods, a series of calibration standards is prepared from reagent material of the compound(s) of interest which span the linear working range. Each of these standards is analyzed using the same conditions as would be used for the actual samples. The response-concentration data pairs are combined into a calibration curve by regression or other methods. The level of the compound in the sample is determined by interpolation within the calibration curve. This method is routinely used for GC/MS.

Direct quantification procedures are recommended for any species which are identified in the hazardous waste incinerator samples. However, direct quantification may not be possible due to a shortage of reference standards, etc., and indirect methods may be necessary in some cases. The most common of the indirect methods is to use the response characteristics of a chemically similar compound to estimate the level of the target constituent of interest. Thus, if for example, benzofluoranthenes were unexpectedly found in a sample but no standard were available, then the level of benzofluoranthenes present in the sample might be estimated from the response curve of benzo(a)pyrene, benzo(e)pyrene, or perylene. Chemical similarity includes similar functionalities, isomeric structures, and homologous series of compounds. The quantitative estimates by this method will be of increasing accuracy as the chemical structure of the reference compound approaches that of the compound of interest. Details of the calibration procedure and calculations are given in Section 5.4 and 6, respectively.

5. Calibration

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm. (0.001 in.). Measure the diameter of the nozzle face opening in 3 separate places (i.e. across 3 different diameters) and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm. (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube/Probe Assembly. The Type S pitot tube probe assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2,[2] or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented or corroded, and meets design and intercomponent spacing specifications.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in Rom.[6] It is recommended that a leak-check be conducted before calibrating the metering system. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. In these cases the following leak-check procedure is suggested: Make a 10-minute calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm). Alternatively, the following procedure is suggested (see Figure 5-1): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in) of water by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in Rom.[6]

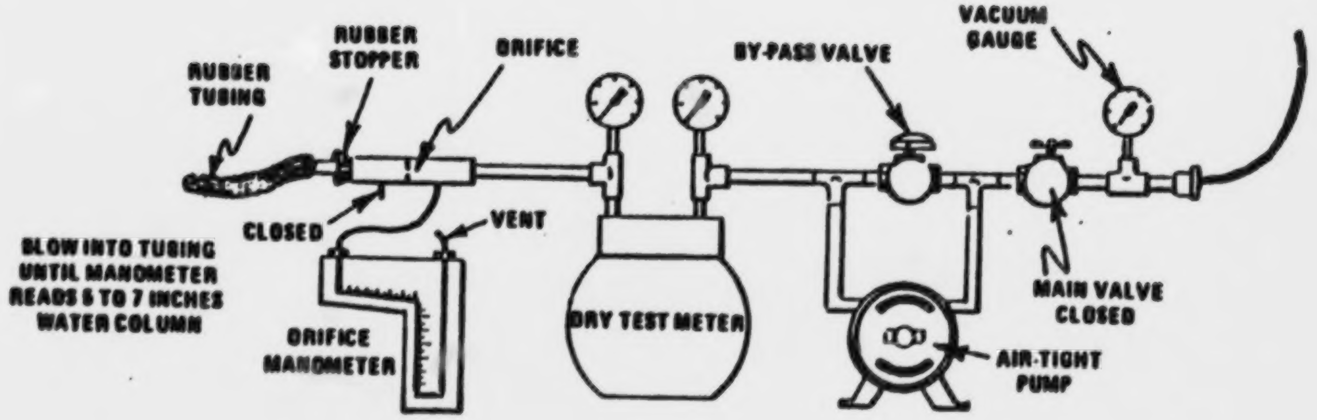

RUBBER TUBING
RUBBER STOPPER
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
BLOW INTO TUBING UNTIL MANOMETER READS 5 TO 7 INCHES WATER COLUMN
CLOSED
VENT
ORIFICE MANOMETER
DRY TEST METER
MAIN VALVE CLOSED
AIR-TIGHT PUMP

Figure 5-1. Meter box leak-check apparatus.

Note: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in Rom.[6] Probes constructed according to Martin[5] need not be calibrated if the calibration curves in Rom[6] are used.

5.5 Temperature Gauges. Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM E-1 #63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5 percent.

5.5.1 Impinger, Organic Module and Dry Gas Meter Thermocouples. For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2® resin bed, a three-point calibration at ice water, room air and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

5.5.2 Probe and Stack Thermocouple. For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water and hot oil bath temperatures must be performed; it is recommended that room air temperature be added as a thermometer and the thermocouple agree to within 1.5 percent at each of the calibration points. A calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

5.6 Aneroid Barometer. Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in Hg) of the mercury barometer, or the corrected barometric pressure value reported by a nearby National Weather Service station. (Same altitude above sea level.)

5.7 Triple-Beam Balance. Calibrate the triple beam balance before each test series using Class-S standard weights; the weights must be within ±0.5 percent of the standards, or the balance adjusted to meet these limits.

5.8 GC/MS. Calibration standards are prepared fresh weekly and run daily. The results are compared to previous runs of the standard (see Section 7, Quality Control for details).

A stock standard is prepared by accurately transferring a known amount of pure compound(s) to a volumetric flask and diluting with methanol. Liquid standards are measured using microliter syringes while solids are conveniently weighed on an analytical balance. The amount (mass) contained in the syringe can be determined by either 1) weighing or 2) utilizing compound density data and the volume. Utilizing the syringe volume method is the most convenient, but care should be excercised to ensure that the most accurate sample is measured. The pure liquid standards should be at room temperature (because most density measurements are made at 20-25°C) and the total syringe volume used should be no less than 10 µL. Care should also be taken not to allow the syringe to warm up (due to body heat) as this will effect the visible measurement of syringe volume. The stock standards should contain all components of interest as well as the compound to be used as the internal standard (see Section 4.4).

Working standards are prepared by diluting aliquots of the stock standard with methanol or other suitable solvent. Again, small volumes are to be avoided, thereby enhancing the accuracy. A calibration curve is developed using a minimum of five standards plus a blank solvent covering a 10-fold range in concentration. This range will be 0 (blank) 0.5X, X, 2X, 5X, and 10X, where X is the minimal detectable amount.

All standards will be stored at sub-ambient temperature and allowed to warm to room temperature before use. Example calculations are given in Section 6.

6. Calculations

6.1 Nomenclature.

A_n = Cross sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the i^{th} component change (i=1, 2, 3.....n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m^3/min (cfm).

M_d = Stack gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lbs/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (21.85 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole, (21.85 in Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature, °K (°R).

T_s = Absolute average stack gas temperature, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry gas meter, m^3 (ft^3).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by EPA Method 2,[2] Equation 2-9, using particulate field data, m/sec (ft/sec).

Y = Dry gas meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Conversion to mm Hg (in Hg) from mm H_2O (in H_2O).

60 = Sec/min.

6.2 Dry Gas Volume at Standard Conditions. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg) by using the equation:

$$V_{m(std)} = V_m Y \quad \frac{T_{std}}{T_m} \times \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}$$

$$= K_1 V_m Y \quad \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in Hg for English units.

Note: This equation can be used as written unless the leakage rate observed during any of the leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, the above equation must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m with the expression:

$$[V_m - \theta (L_p - L_a)]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m by the expression:

$$[V_m - \theta_1 (L_1 - L_a)] - \sum_{i=2}^{n} [\theta_i (L_i - L_a) - \theta_p (L_p - L_a)]$$

and substitute only those leakage rates (L_i or L_p) which exceed L_a.

6.3 Moisture Content.

6.3.1 Volume of Water Vapor.

$$V_{w(std)} = V_{1c} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c}$$

where:

K_2 = 0.001333 m³/mL for metric units.
= 0.04707 ft³/mL for English units.

6.4 Isokinetic Variation.

6.4.1 Calculation from Unreduced Data.

$$I = \frac{100\ T_s\ [K_3 F_{1c} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60 \theta V_s P_s A_n}$$

where:

K_3 = 0.003454 mm Hg-m³/mL-°K for metric units.
= 0.002669 in Hg-ft³/mL-°R for English units.

6.4.2 Calculation from Intermediate Values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} v_s \theta A_n P_s 60 (1-B_{ws})}$$

$$= \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1-B_{ws})}$$

where:

K_4 = 4.320 for metric units.
= 0.09450 for English units.

6.4.3 Acceptable Results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable.

6.5 Concentration of Any Given POHC Per Sample. An average relative response factor (RRF) for a given internal standard is calculated in the following way.

1) Obtain an area count for each compound from injections of each of the five levels of calibration standards. Each standard contains a known amount of the POHC's of interest plus a known amount of the quantitation standard. The area for each compound is based on a preselected ion (usually the major ion). For the quantitation standard, d_{10}-phenanthrene, the major ion is 188.

2) Calculate a relative response factor in triplicate for each compound at each concentration level using the equation below.

$$RRF = \frac{A_s C_{is}}{A_{is} C_s}$$

where:

A_s = Area of the characteristic ion for the POHC to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Concentration of the internal standard (μg/mL).
C_s = Concentration of the POHC (μg/mL) to be measured.

3) Average the average RRF's for each compound from each level calculating a grand average RRF for each compound. If RRF mean exhibits a % CV >0, a linear regression may be used.

The concentration of any give POHC is calculated using the equation given below:

$$\frac{C_{is}}{A_{is}\text{ (major ion)}} \times \frac{A_{unk\text{ (major ion)}}}{RRF} = C_{unk}(\mu g/mL)$$

where:

A_{unk} = Area of the major ion for the POHC of interest.
A_{is} = Area of the major ion for the internal standard.
C_{is} = Concentration of the internal standard spiked into the sample (μg/mL).
C_{unk} = Concentration of the unknown (μg/mL).
RRF = Average relative response factor of the POHC of interest.

6.6 Concentration of any Given POHC in the Gaseous Emissions of a Combustion Process.

1) Multiply the concentration of the POHC as determined in Section 6.5 by the final concentration volume, typically 10 mL.

$$C_{unk}\ (\mu g/mL) \times \text{sample volume (mL)} = \text{amount } (\mu g) \text{ of POHC in sample}$$

2) Sum the amount of POHC found in all samples associated with a single train.

$$\text{Total } (\mu g) = \text{XAD-2}^{\circledR}\ (\mu g) + \text{condensate } (\mu g) + \text{rinses } (\mu g) + \text{impinger } (\mu g)$$

3) Divide the total μg found by the volume of stack gas sampled (m^3).

$$\text{Total } \mu g/\text{train sample volume} = \text{concentration of POHC } (\mu g/m^3)$$

6.7 Percent Recovery. Divide the amount of any single surrogate spiked into a sample before sample work-up into the amount of that surrogate found to be in sample after analysis. Then convert to a percent.

$$\frac{\text{Amount of spike found after analysis}}{\text{Amount of spike into a sample}} \times 100 = \%\ \text{recovery.}$$

7. Quality Control.

Table 7-1 presents the major components of the quality control for this method.

7.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

7.2 Analysis. The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices.

The assessment of combustion data, positive identification and quantitation of the selected compounds are dependent on integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

7.2.1 Field Blanks. The field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, and unused filters and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area and leak checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

7.2.2 Method Blanks. A method blank must be prepared for each set of analytical operations to evaluate contamination and artifacts that can be derived from glassware, reagents and sample handling in the laboratory.

Table 7-1. QUALITY ASSURANCE PROCEDURES FOR TRACE ORGANIC ANALYSIS

Field blanks	1 - Flue gas sampling train per day 10% - Filter returned unused 10% - Resin cartridges returned unused 1 - Field solvent blanks per lot 3 - Sample containers used
Method blanks	1 - Analytical method blank
Method validations	Method procedures studied and validated with spiked blanks and spiked samples prior to initiating analysis program
Surrogate spiking compounds	Dioxane-d_8, pyridine-d_5, toluene-d_8, chlorobenzene-d_5, phenol-d_5, nitrobenzene-d_5, naphthalene-d_8, and pentachlorophenol-$^{13}C_6$ spiked in all samples prior to extraction to provide recovery and precision data. In addition where available labeled analogs of the POHC of interest should be spiked.
Column performance mixture	Grob test mixture to evaluate and identify capillary column characteristics.
Internal standards for quantitation	Phenanthrene-d_{10}
Performance tests	Interlaboratory testing/split samples and/or performance audit samples

7.2.3 Method Performance Evaluation. Evaluation of analytical procedures for a selected series of compounds must include the sample preparation procedures, and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

7.2.4 Capillary Column Performance Tests. Capillary columns will be evaluated and characterized utilizing Grob type mixtures. The columns will be evaluated on installation and at least once per week thereafter. In addition if column performance deteriorates, steps must be taken to improve the performance or the column must be replaced.

7.2.5 Surrogate Spiking Compounds. The number of samples required to establish the precision and accuracy of a method can be significantly reduced by utilizing surrogate compounds as performance indicators. By utilizing stable isotope-labeled compounds, method performance can be monitored on a routine basis without the cost of additional spiked analyses. Stable isotope-labeled compounds that have the same physical and chemical characteristics as the analyte and that are not present in the samples are ideal choices for determining method performance.

The recoveries of the stable isotope labeled surrogate compounds are used as the primary measurement of method analysis precision. In addition, the spiking of surrogate standards in all sample field blanks, method blanks and actual samples prior to extractions can be used to determine whether any sample matrix effects or other analytical problems affect the accuracy of the analyses.

7.3 Quantitative Analysis. Quantitative analytical methods are used to estimate the level of hazardous compounds in various matrices. The process of estimation or quantitation requires the precision, accuracy (bias), and detection limit of the analytical method to be known and documented.

7.3.1 Calibration.

1) Initial calibration standards are to be prepared and analyzed in the concentration series 0 (blank), 0.5X, X, 2X, 5X, and 10X where X is the concentration in the solvent being analyzed corresponding to the required or desired detection limit in the original matrix.

2) Daily Calibration. An instrument calibration standard will be run prior to analyses each day to establish that the sensitivity of the instrument has not changed over the working range. Data generated will be compared against the cumulative data to date to establish the stability of the instrument response.

3) Quality control samples are to be inserted at random in a sample analysis series. At least one control sample is to be included with each lot of samples. The types of control samples are chosen to minimize the number of control samples and maximize the quality control data obtained from the analytical system. For example, a spike of a previously analyzed combustion sample or blank XAD-2® extract containing no detectable analyte may exhibit matrix effects that will not be demonstrated by a spike in a standard solvent.

4) Data generated from daily control samples are to be used to update control charts and, by addition to the existing data base, to refine the detection limit of the analytical method as well as the estimates of precision and accuracy.

5) Concentration values less than the average detection limit of the method will be reported as "less than" the detection limit unless sufficient data exist to justify a lower detection limit. Conversely, detection limits higher than the average detection limit (as is the case of a sample with high background interferences) will be reported as "less than" the higher detection limit.

7.4 Optimization of the GC/FID and GC/MS Procedures. GC operating conditions will be optimized by analyzing solutions containing a variety of the candidate POHCs by the GC/FID technique. The column head pressure is adjusted appropriately to maximize the FID response to the test mixtures. These adjustments are used to select the optimum carrier gas velocity.

Having established GC operating conditions by the GC/FID procedure, the method is then applied to the determination of the candidate POHCs by GC/MS. The mass spectrometer is operated in full scan (40 to 450 amu) in the EI mode. The scan time is maintained at ≤1 s to enable the collection of enough scans to characterize each capillary GC peak.

7.5 GC Quality Control Procedures. The GC/FID and GC/MS procedure will include calibration utilizing standard solutions of the candidate POHCs. Five-point calibration curves are prepared for each candidate POHC determined by gas chromatography. Each response of the FID and/or MS response (relative to phenanthrene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column will be plotted.

In addition to the use of standards for the calibration, the performance of the GC/MS system is checked daily with decafluorotriphenylphosphine (DFTPP) according to the requirements given in EPA Method No. 625. The performance criteria listed in Table 4-2 will be met.

The precision of determinations by GC/FID and GC/MS is assessed by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD) calculated from Equation 1

$$\text{RSD } (\%) = \frac{\text{SD}}{\bar{X}} 100 \qquad (1)$$

Standard Deviation (SD) is calculated from Equation 2

$$\text{SD} = \left[\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{(n-1)} \right]^{\frac{1}{2}} \qquad (2)$$

Mean relative response ($\bar{X}$) is calculated from Equation 3

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

where:

n = Number of replicate measurements.

X_i = Relative response of the POHC standard.

Phenanthrene-d_{10} will be used as an internal standard in all GC methods. Along with the analytes phenanthrene-d_{10} will be injected to minimize the effect of injection volume and instrument performance upon the precision of determinations. Also, the phenanthrene-d_{10} internal standard is used to calculate the relative response factor (RRF) for each POHC from Equation 4.

$$RRF = (A_s C_{is})/(A_{is} C_s) \quad (4)$$

where:

A_s = Area of the characteristic ion for the POHC to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Concentration of the internal standard (μg/mL).
C_s = Concentration of the POHC (μg/mL) to be measured.

7.6 Statistical Analysis of Data.

7.6.1 Found Concentration.

1) Instrument calibration standards to cover the range of anticipated concentrations are prepared. These calibration standards are introduced to the instrument to obtain responses for the various concentrations.

2) An instrument calibration curve is constructed by plotting the response versus the calibration standard concentration and determining the best fit regression curve for the data. A measure of the linearity of the responses is the correlation coefficient. The mean of the values obtained will be used instead of a regression if the values agree within 10 percent.

3) The found concentration from the analysis of a sample is obtained by entering the instrument calibration curve with the sample response and reading the corresponding concentration. The concentration read from the calibration curve must be modified to reflect the concentration in the original matrix assuming 100 percent recovery through the analytical method. The resultant concentration is the found concentration.

7.6.2 Detection Limit.

1) Before any analytical system is employed in a determination, sufficient spikes and blanks will be run to statistically establish the lowest concentration which may be distinguished from zero. The lowest calculated concentration will be reported as the detection limit of the method provided that at least one of the spike (target) concentrations is below the calculated detection limit. Otherwise, the lowest spike concentration is the minimum level that can be reported as the detection limit. The highest spike concentration will represent the upper limit of reportable data.

2) The detection limit is derived from the assumption that the relationship between the found concentration and target concentration is linear, and that the variance about the least squares linear regression line is homogeneous over the tested concentration range, and that the distribution of found concentrations for a given target concentration is a normal distribution.

Based on these assumptions, the least squares linear regression line of the form, $y = y_o + bx$, is determined, where:

y_o = y axis (found concentration) intercept.

b = Slope of the line.

x = Target concentration.

A measure of the linearity of the data is the correlation coefficient. The confidence limits about the regression line are given by:

$$y = yo + bx + s\, t_{(n-2),\ (1-\alpha/2)} \left(\frac{1}{n} + \frac{(x-\bar{x})^2}{\Sigma(x_i-\bar{x})^2} \right)^{\frac{1}{2}}$$

for the upper confidence limit and

$$y = yo + bx - s\, t_{(n-2),\ (1-\alpha/2)} \left(\frac{1}{n} + \frac{(x-\bar{x})^2}{\Sigma(x_i-\bar{x})^2} \right)^{\frac{1}{2}}$$

for the lower confidence limit, where:

$$s = [[\Sigma y^2 i - a\Sigma yi - b\Sigma xiyi]/(n-2)]^{\frac{1}{2}}$$

where:

$t_{(n-2),\ (1-\alpha/2)}$ = Student's t for (n-2) degrees of freedom and a level of significance of α, and

n = total number of data points.

The detection limit, x_d, is the value of x corresponding to a point on the lower confidence limit curve where the value of y equals the value of y on the upper confidence limit curve at x = 0.

7.6.3 Documentation Surrogate (Target) Recoveries. Each sample fraction that is analyzed will be spiked with the following surrogate (see Table 7-2) compounds at 10X where X is the minimum detectable level for the individual compound. In addition where readily available stable labeled analogs of the POHC's being incinerated should be spiked in the indirect fractions at levels based on the following: (1) target detection limits for the selected POHC's and (2) expected concentrations of the organic waste components. For example, incineration effluent samples would require spiking levels of labeled compounds at 2 to 10 times the detection limit required to measure 99.99% DRE of the POHCs.

Data generated will be compiled in Table 7-2 and treated as shown in Table 7-3. Surrogate recovery will be for the total sample, i.e., the average found value for all fractions of a sampling train, and treated for each individual fraction.

Table 7-2. SURROGATE DATA

Surrogate(s)	Target concentration 10X, where X equal MDL	Organic rinse(s) 1	Condensate 2	Impingers 3	XAD_2/ filter 4
Dioxane-d_8	250 µg[a]				
Pyridine-d_5	250 µg				
Toluene-d_8	250 µg				
Chlorobenzene-d_5	250 µg				
Phenol-d_5	250 µg				
Nitrobenzene-d_5	250 µg				
Naphthalene-d_8	250 µg				
Pentachlorophenol-$^{13}C_6$	250 µg				

[a] Total µg based on an assumed MDL of 25 ng on-column;

10 mL concentrate = 25 ng/µL on-column

1 mL concentrate = 250 ng/µL on-column

Table 7-3. SURROGATE RECOVERIES

Surrogate(s)	Target concentration (μg)	Average found value	Standard deviation	Percent imprecision	Percent inaccuracy
Dioxane-d_8	250				
Pyridine-d_5	250				
Toluene-d_8	250				
Chlorobenzene-d_5	250				
Phenol-d_5	250				
Nitrobenzene-d_5	250				
Naphthalene-d_8	250				
Pentachlorophenol-$^{13}C_6$	250				

$$\text{Percent relative standard deviation} = \frac{S}{\bar{X}} \times 100$$

where:

S = Standard deviation.

$\bar{X}$ = Average found concentraton.

$$\text{Percent recovery} = \frac{\bar{X}}{TC} \times 100$$

where:

$\bar{X}$ = Average found concentration of the TC.

TC = Target concentration.

8. References

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APPENDIX A-1
CLEANING OF GLASSWARE

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling train components, or any other glassware coming in contact with an extract that will be evaporated to a lesser volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contamination substance, resulting in extraneous chromatographic peaks that, in extreme cases, may completely overlap and mask peaks of interest.

Although chemists do not all agree on procedural details in the cleaning of glassware, the majority are in agreement regarding the basic cleaning steps. These are:

1. removal of surface residuals immediately after use;
2. hot soak to loosen and flotate most particulate material;
3. hot water rinse to flush away flotated particulate;
4. soak with oxidizing agent to destroy traces of organic compounds;
5. hot water rinse to flush away materials loosened by deep penetrant soak;
6. distilled water rinse to remove metallic deposits from the tap water; and
7. methanol rinse to flush off any final traces of organic materials and remove the water.

Each of these eight fundamental steps will be discussed in the order in which they appear above.

1. As soon as possible after use of glassware coming in contact with sample, i.e., beakers, pipets, flasks, or bottles used for standards, the glassware should be methanol-flushed before placing in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40 to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157", manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex", a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers, and bottle caps can be wrapped in aluminum foil and oven-dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an option, the glassware can be heated to a minimum of 300°C to vaporize any organics.

APPENDIX A-2

PREPARATION OF XAD-2® SORBENT RESIN

1. SCOPE AND APPLICATION

XAD-2® resin, as supplied by the manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions followed by careful drying.

2. EXTRACTION

2.1 Method 1

The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2®. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse - place resin in a beaker and rinse once with D.I. water and discard. Fill with water a second time and let stand overnight and discard.
Water	Extract with H_2O for eight hours.
Methyl alcohol	Extract for 22 hours.
Methylene chloride	Extract for 22 hours.
Methylene chloride (fresh)	Extract for 22 hours.

2.2 Method 2

As an alternative to Soxhlet extraction, a continuous extractor has also been fabricated for the extraction sequence and is described in Figure B-1. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-2-1 contains about 500 g of finished XAD-2®. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2® is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3 L in this case) to hold solvent equal to twice the dead volume of the XAD-2® canister. Solvent is refluxed through the Snyder column and the distillate continuously cycled up through the XAD-2® for extraction and returned to the flask. The flow is maintained upwards through the XAD-2® for extraction and returned to the flask. The flow is maintained upwards through the XAD-2® to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore, the aqueous rinse is accomplished by simply flushing the canister with about 20 L of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hour period is normally sufficient for each extraction.

All materials of construction are glass, Teflon®, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3. DRYING

After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

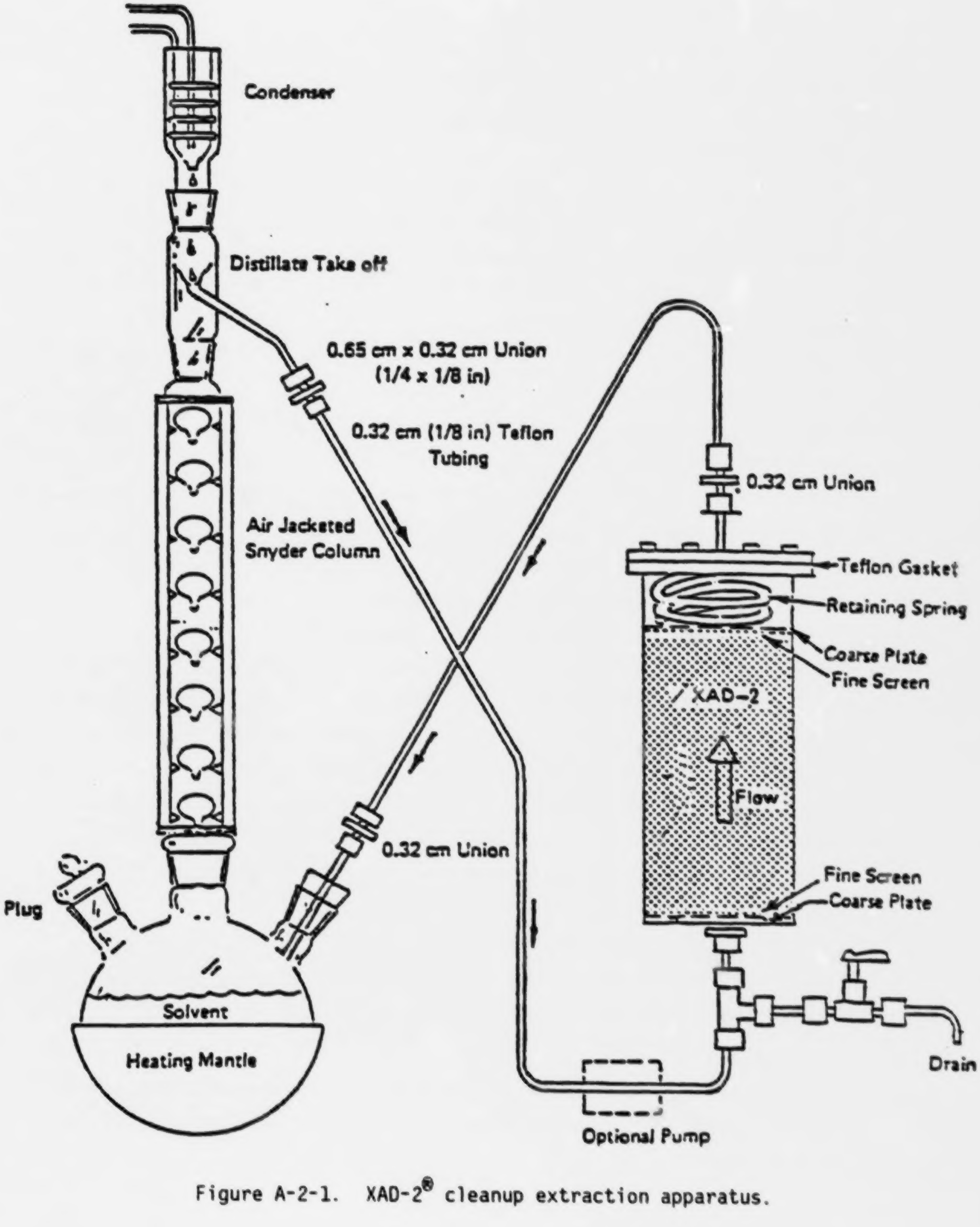
Condenser
Distillate Take off
0.65 cm x 0.32 cm Union
(1/4 x 1/8 in)
0.32 cm (1/8 in) Teflon
Tubing
Air Jacketed
Snyder Column
0.32 cm Union
Teflon Gasket
Retaining Spring
Coarse Plate
Fine Screen
XAD-2
Flow
0.32 cm Union
Fine Screen
Coarse Plate
Plug
Solvent
Heating Mantle
Drain
Optional Pump

Figure A-2-1. XAD-2® cleanup extraction apparatus.

A simple column with suitable retainers as shown in Figure A-2-2 will serve as a satisfactory column. A 10.2-cm (4-in) Pyrex® pipe 0.6 m (2 ft) long will hold all of the XAD-2® from the extractor shown in Figure B-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.1 Method 1

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2®. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2® may be dried overnight consuming a full 160-L cylinder of liquid nitrogen.

3.2 Method 2

As a second choice, high purity tank nitrogen may be used to dry the XAD-2®. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4. QUALITY CONTROL PROCEDURES

For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be re-extracted as discussed in Section 3.2.1 if the residual extractable organics are greater than 20 μg/mL by TCO analysis, or the gravimetric residue is greater than 0.5 mg/20 g XAD-2® extracted.

Four control procedures are used with the final XAD-2® to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS as described in Section 4.4, and (4) residue (GRAV).

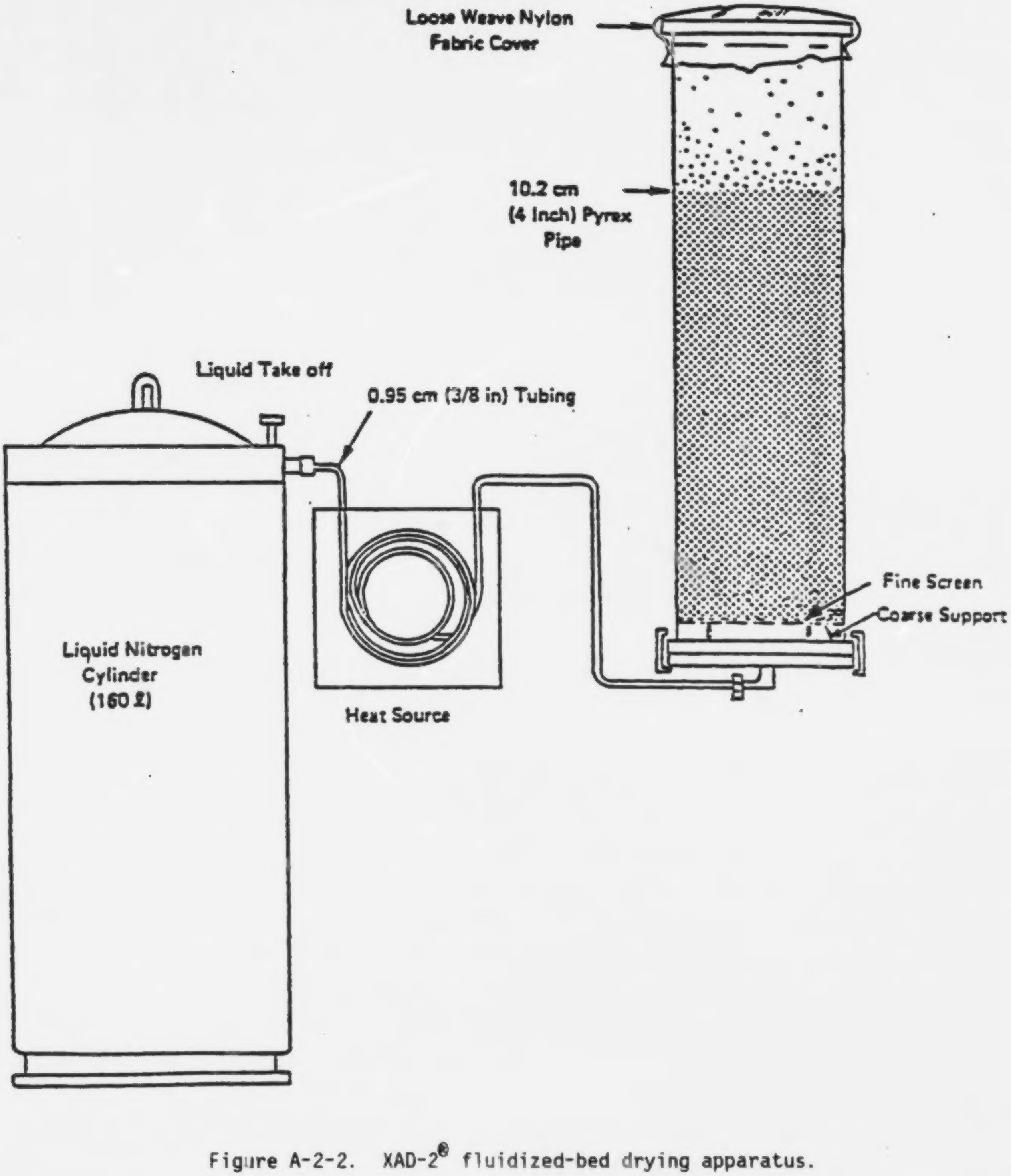
Loose Weave Nylon Fabric Cover
10.2 cm (4 Inch) Pyrex Pipe
Liquid Take off
0.95 cm (3/8 in) Tubing
Fine Screen
Coarse Support
Liquid Nitrogen Cylinder (160 ℓ)
Heat Source

Figure A-2-2. XAD-2® fluidized-bed drying apparatus.

4.1 Procedure for Residual Methylene Chloride

4.1.1 Description. A 1 ±0.1 g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five microliters of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared to a reference standard.

The reference solution consists of 2.5 μL of methylene chloride in 100 mL of toluene, simulating 100 μg residual methylene chloride on the resin. The acceptable maximum content is 1,000 μg/g resin.

4.1.2 Experimental.

- 6 ft x 1/8 in SS column containing 10 percent OV-101 on 100/120 Supelcoport.
- Helium carrier at 30 mL/minute.
- FID operated on 4×10^{-11} A/mV.
- Injection port temperature: 250°C.
- Detector temperature: 305°C.
- Programmed: 30°C(4 min) 40°/min 250°C (hold).
- Program terminated at 1,000 seconds.

4.2 Procedure for Residual Extractable Organics

4.2.1 Description. A 20 ±0.1 g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned, glass wool. (Note that 20 g of resin will fill a thimble, and the resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hours with 200 mL of pesticide-grade methylene chloride.*

The 200-mL extract is reduced in volume to 10 mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five microliters of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain more than 20 μg/mL of TCO extracted from the XAD-2®. This is equivalent to 10 μg/g of TCO in the XAD-2® and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2® module. Care should be taken to correct the TCO data for a solvent blank prepared (200 → 10 mL concentration) in a similar manner.

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*Burdick and Jackson pesticide grade or equivalent purity.

4.2.2 Experimental. Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.3 GC/MS Screen

The extract, as prepared in 4.2, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Section 4.4 of Appendix A. The extract is screened at the MDL of each compound. The presence of any compound at a concentration greater than 25 μg/mL in the concentrated extract will require the XAD-2® to be re-cleaned by repeating the methlyene chloride step.

4.4 Methodology for Residual Gravimetric Determination

After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be less than 0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 μg/g in the XAD-2® or about 3.25 mg in a resin charge of 130 g.

APPENDIX A-3

MS - ANALYTICAL IONS

This appendix lists the Appendix VIII Hazardous Constituents (according to the May 20, 1981 Federal Register) that are analyzed by GC/MS procedures with the appropriate MS analytical ions and their corresponding intensities.

MS - ANALYTICAL IONS

Compound	Ions (Intensities)
Acetonitrile	41(100), 40(50), 39(17), 38(5)
Acetophenone	105(100), 77(83), 51(31), 120(25)
2-Acetylaminofluorene	181(100),180(82), 223(62), 152 (37)
Acrolein	56(72), 27(100), 26(54), 55(51)
Acrylamide	27(100), 44(89), 71(72), 55(58)
Acrylonitrile	53(100), 26(93), 52(79), 51(30)
Aldrin	66(100), 263(73), 220(11)
Allyl alcohol	57(100), 29(39), 31(32), 58(26)
4-Aminobiphenyl	169(100), 170(14), 168(11), 84.5(9)
5-(Aminomethyl)-3-isoxazolol	98(100), 41(66), 39(49), 67(23)
Amitrole	28(100), 84(66), 57(28), 29(23)
Aniline	93(100), 66(33), 65(18), 39(18)
Aramite	
Auramine	
Benz(c)acridine	229(100), 228(19), 230(19), 201(10)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Benz(a)anthracene	228(100), 229(19), 226(19), 114(18)
Benzene	78(100), 77(19), 52(16), 51(15)
Benzene, dichloromethyl-	
Benzenethiol	110(100), 66(38), 39(28), 109(25)
Benzidine	184(100), 185(15), 183(11), 92(8)
Benzo(b)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(j)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(a)pyrene	252(100), 250(25), 253(23), 125(21)
p-Benzoquinone	108 (100), 54(99), 82(37), 53(32)
Benzotrichloride	159(100), 161(64), 89(14), 163(11)
Benzyl chloride	91(100), 126(28), 65(9), 92(8)
Bis(2-chloroethoxy)methane	93(100), 63(65), 95(32), 27(22)
Bis(2-chloroethyl) ether	93(100), 63(98), 27(75), 95(32)
N,N-Bis(2-chloroethyl)-2-naphthylamine	
Bis(2-chloroisopropyl) ether	45(100), 43(36), 41(34), 77(19),
Bis(chloromethyl)ether	79(100), 49(47), 81(33), 51(16)
Bis(2-ethylhexyl) phthalate	149(100), 57(54), 169(33), 71(27)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Bromoacetone	43(100), 15(84), 14(19), 79(13)
Bromomethane	94(100), 96(94), 15(47), 93(21)
4-Bromophenyl phenyl ether	248(100), 250(99), 141(45), 77(32)
Brucine	
2-Butanone peroxide	
Butyl benzyl phthalate	149(100), 91(50), 206(18), 104(12)
2-sec-Butyl-4,6-dinitrophenol (DNBP)	
Carbon disulfide	76(100), 32(22), 44(17), 78(9)
Carbon oxyfluoride	47(100), 66(55), 28(14), 31(4)
Chloral	*
Chlordane (alpha and gamma isomers)	373(19), 375(17), 377(10)
Chlorinated benzenes, N.O.S.	112(100), 77(45), 114(33), 51(12)
Chlorinated ethane, N.O.S.	64(100), 28(91), 29(84)
Chlorinated fluorocarbons, N.O.S.	**
Chlorinated naphthelene, N.O.S.	162(100), 164(33), 127(30)
Chlorinated phenol, N.O.S.	128(100), 130(33), 65(24)
Chloroacetaldehyde	*
Chloroalkyl ethers	**
p-Chloroaniline	127(100), 65(34), 129(31), 92(20)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensitites)
Chlorobenzene	112(100), 77(45), 114(33), 51(12)
Chlorobenzilate	
p-Chloro-m-cresol	142(100), 107(80), 144(32), 77(24)
1-Chloro-2,3-epoxypropane	
2-Chloroethyl vinyl ether	63(100), 27(62), 43(42), 44(38)
Chloroform	83(100), 85(64), 47(37), 35(20)
Chloromethane	50(100), 52(32), 15(21), 49(9)
Chloromethyl methyl ether	45(100), 29(25), 15(22), 49(17)
2-Chloronaphthalene	162(100), 164(33), 127(33), 128(17)
2-Chlorophenol	128(100), 130(33), 65(24), 64(12)
3-Chloropropionitrile	49(100), 54(77), 51(39). 53(26)
Chrysene	228(100), 226(26), 229(21), 114(13)
Coal Tars	**
Creosote	**
Cresols	**
Crotonaldehyde	*
2-Cyclohexyl-4,6-dinitrophenol	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
DDD	235(100), 237(66), 165(38), 75(21)
DDE	246(100), 318(83), 316(66), 248(58)
DDT	235(100), 237(72), 165(59),75(22)
Diallate	
Dibenz(a,h)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,j)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,h)anthracene	278(100), 139(24), 279(16), 276(16)
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	302(100)
Dibenzo(a,h)pyrene	302(100)
Dibenzo(a,i)pyrene	302(100)
1,2-Dibromo-3-chloropropane	157(100), 155(78), 75(46), 159(25)
1,2-Dibromomethane	107(100), 109(95), 27(54), 28(11)
Dibromoethane	174(100), 93(72), 95(62), 172(52)
Di-n-butyl phthalate	149(100), 41(28), 29(25), 28(22),
Dichlorobenzene (meta, ortho and para isomers)	146(100) 148(62), 111(39), 75(23)
Dichlorobenzene, N.O.S.	146(100), 148(62), 111(39), 75(23)
3,3'-Dichlorobenzidine	252(100), 254(67), 256(10), 126(12)
1,4-Dichloro-2-butene	75(100), 89(48), 53(36), 77(33)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dichlorodifluoromethane	
1,1-Dichloroethane	63(100), 27(72), 65(33), 83(12)
1,2-Dichloroethane	62(100), 64(33), 27(70)
trans-1,2-Dichloroethene	61(100), 96(80), 98(51), 63(29)
Dichloroethylene, N.O.S.	146(100), 148(62), 111(38), 113(13)
1,1-Dichloroethylene	61(100), 96(80), 98(52), 63(33)
Dichloromethane	49(100), 84(72), 86(44), 51(31)
2,4-Dichlorophenol	162(100), 164(65), 63(65), 98(40)
2,6-Dichlorophenol	162(100), 164(64), 63(29), 126(20),
2,4-Dichlorophenoxyacetic acid (2,4-D)	162(100), 220(78), 164(64), 222(49)
Dichloropropane, N.O.S.	63(100), 62(74), 27(41), 41(34)
1,2-Dichloropropane	79(100). 81(38). 43(27). 49(20)
Dichloropropanol, N.O.S.	
Dichloropropene, N.O.S.	75(100), 77(33), 110(25), 112(15)
1,3-Dichloropropene	75(100), 39(55), 77(32), 49(26)
Dieldrin	79(100), 108(19), 263(18), 277(18)
1,2:3,4-Diepoxybutane	55(100), 44(91), 43(73), 29(65)
N,N-Diethylhydrazine	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
0,0-Diethyl S-methyl ester of phosphordithioic acid	
0,0-Diethylphosphoric acid, O-p-nitrophenyl ester	
Diethyl phthalate	149(100), 177(28), 150(13), 176(9)
0,0-Diethyl 0-2-pyrazinyl phosphorothioate	
Dihydrosafrole	163(100), 164(25), 77(19), 51(12)
Diisopropylfluorophosphate	
Dimethoate	
3,3'-Dimethoxybenzidine	244(100), 184(61), 201(38), 229(21)
p-Dimethylaminoazobenzene	120(100), 225(73), 77(58), 42(38)
7,12-Dimethylbenz(a)anthracene	256(100), 241(70), 257(48), 240(46)
3,3'-Dimethylbenzidine	
1,1-Dimethylhydrazine	60(100), 42(51), 59(45), 45(42)
1,2-Dimethylhydrazine	60(100), 42(98), 28(53), 45(52)
alpha,alpha-Dimethylphenethylamine	58(100), 91(7), 59(5), 134(3)
2,4-Dimethylphenol	122(100), 107(90), 121(55), 91(20)
Dimethyl phthalate	163(100), 77(19), 164(10), 194(6)
Dimethyl sulfate	15(100), 29(71), 95(66), 31(66)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dinitrobenzene, N.O.S.	30(100), 75(75), 168(70), 76(52)
4,6-Dinitro-o-cresol and salts	
2,4-Dinitrophenol	
2,4-Dinitrotoluene	165(100), 89(65), 90(26), 63(35)
2,6-Dinitrotoluene	165(100), 89(52), 90(35), 148(22)
Di-n-octyl phthalate	149(100), 57(39), 167(32), 279(2)
1,4-Dioxane	28(100), 29(32), 59(24), 88(22)
Diphenylamine	
1,2-Diphenylhydrazine	77(100), 182(29), 105(23), 93(15)
Di-n-propylnitrosamine	70(100), 42(99), 117(79), 43(65)
Disulfoton	
2,4-Dithiobiuret	
Endosulfan	201(100), 283(48), 278(30)
Endrin and metabolites	81(100), 263(70), 82(61)
Ethyl carbamate	
Ethyleneimine	42(100), 43(62), 28(59), 15(22)
Ethyl methacrylate	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Ethyl methansulfonate	79(100), 109(78), 97(26), 80(19)
Fluoroanthene	202(100), 200(20), 203(18), 101(13)
Fluoroacetic acid, sodium and salt	
Formaldehyde	*
Formic acid	
Glycidylaldehyde	*
Halomethane, N.O.S.	**
Heptachlor	100(100), 272(60), 274(46)
Heptachlor epoxide (alpha, beta and gamma isomers)	355(100), 353(79), 351(60)
Hexachlorobenzene	284(100), 286(80), 282(53), 142(29)
Hexachlorobutadiene	225(100), 227(65), 223(63), 260(38)
Hexachlorocyclohexane (all isomers)	181(100), 183(99), 109(80), 217(78)
Hexachlorocyclopentadiene	
Hexachloroethane	117(100), 119(95), 199(50), 201(85)
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	
Hexachlorophene	
Hexachloropropene	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Hexaethyl tetraphosphate	
Hydrazine	32(100), 31(47), 29(40), 30(31)
Indeno(1,2,3-c,d)pyrene	276(100), 138(38), 277(26), 274(21)
Iodomethane	142(100), 127(38), 141(14), 15(13)
Isocyanic acid, methyl ester	
Isobutyl alcohol	
Isosafrole	162(100), 104(42), 131(30), 103(28)
Kepone	
Maleic anhydride	26(100), 54(62), 25(61), 28(36)
Maleic hydrazide	
Malononitrile	66(100), 38(34), 39(34), 28(31)
Methyacrylonitrile	
Methanethiol	
Methapyrilene	58(100), 97(71), 72(22), 71(19)
Methoxychlor	
2-Methylaziridine	28(100), 56(80), 57(54), 30(37)
3-Methylcholanthrene	256(100)
4,4'-Methylenebis-(2-chloroaniline)	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Methyl ethyl ketone (MEK)	43(100), 29(24), 72(17), 27(16)
Methyl hydrazine	46(100), 45(61), 28(58), 31(41)
2-Methyllactonitrile	
Methyl methacrylate	41(100), 69(83), 100(51), 39(36)
Methyl methanesulfate	
N-Methyl-N'-nitro-N-nitrosoquanidine	
Methyl parathion	
Methylthiouracil	
Naphthalene	128(100), 127(20), 129(18), 64(7)
1,4-Naphthoquinone	158(100), 104(39), 76(34), 102(31)
1-Naphthylamine	143(100), 115(45), 116(25), 144(14)
2-Naphthylamine	143(100), 115(38), 144(14), 116(13)
Nicotine and salts	84(100), 133(27), 42(20), 162(19)
p-Nitroaniline	138(100), 92(50), 108(33), 65(30)
Nitrobenzene	77(100), 128(55), 51(55), 65(25)
Nitroglycerine	46(100), 30(24) 29(15), 76(9)
4-Nitrophenol	65(100), 139(90), 109(72), 81(33)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Nitrosamine, N.O.S.	**
N-Nitrosodi-n-butylamine	84(100), 57(79), 29(53), 41(52)
N-Nitrosodiethanolamine	
N-Nitrosodiethylamine	43(100), 42(68), 44(60), 56(56)
N-Nitrosodimethylamine	74(100), 42(75), 43(40), 44(10)
N-Nitroso-N-ethylurea	
N-Nitrosomethylethylamine	88(100), 42(93), 43(46), 56(24)
N-Nitroso-N-methylurea	
N-Nitroso-N-methylurethane	43(100), 96(76), 66(28), 79(20)
N-Nitrosomethylvinylamine	
N-Nitrosomorpholine	56(100), 116(55), 86(37), 28(13)
N-Nitrosonornicotine	
N-Nitrosopiperidine	42(100), 114(91), 55(56), 56(24)
N-Nitrosopyrrolidine	100(100), 41(61), 42(58), 68(16)
N-Nitrososarcosine	
5-Nitro-o-toluidine	
Octamethylpyrophosphoramide	

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	
Paraldehyde	*
Parathion	
Pentachlorobenzene	250(100), 252(62), 248(62), 108(41)
Pentachloroethane	117(100), 119(96), 167(95), 95(93)
Pentachloronitrobenzene (PCNB)	
Pentachlorophenol	266(100), 264(62), 268(63), 165(54)
Phenol	94(100), 66(19), 65(17)
Phenylenediamine	
Phosphorodithioic acid, 0,0-diethyl S-((ethylthio) methyl)ester [Phorate]	
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethylamino)sulfonyl)phenyl)ester [Famphur]	
Phthalic acid esters, N.O.S.	**
Phthalic anhydride	104(100), 76(84), 50(40), 148(39)
2-Picoline	
Polychlorinated biphenyl, N.O.S.	**
Pronamide	
1,3-Propane sultone	
n-Propylamine	
Propylthiouracil	

MS ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
2-Propyn-1-ol	55(100), 39(8), 28(6), 29(5)
Pyridine	79(100), 52(71), 51(36), 50(26)
Resorcinol	
Saccharin and salts	183(100), 76(99), 50(72), 120(40)
Safrole	162(100), 131(38), 104(31), 135(26)
1,2,4,5-Tetrachlorobenzene	216(100), 214(79), 218(49), 179(15)
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	322( ), 320( )
Tetrachloroethane, N.O.S.	
1,1,1,2-Tetrachloroethane	83(100), 85(66), 131(7), 133(7)
1,1,2,2-Tetrachloroethane	131( ), 133( ), 117( ), 119( )
Tetrachloroethene	166(100), 164(78), 129(64), 131(62)
Tetrachloromethane	
2,3,4,6-Tetrachlorophenol	
Tetraethyldithiopyrophosphate	
Tetraethylpyrophosphate	
Tetranitromethane	
Toluene	92(65), 91(100), 65(12), 51(6)

MS ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Toluenediamine	121(100), 122(93), 94(17), 105(13)
Toluene diisocyanate	174(100), 145(40), 28(39), 27(38)
Toxaphene	231( ), 233( ), 235( )
Tribromomethane	173(100), 171(50), 175(49), 93(22)
1,2,4-Trichlorobenzene	180(100), 182(95), 184(30), 145(30)
1,1,1-Trichloroethane	97(100), 99(66), 117(17), 119(16)
1,1,2-Trichloroethane	97(100), 83(95), 99(66), 85(60)
Trichloroethene	95(100), 130(90), 132(85), 97(66)
Trichloromethanethiol	
Trichloromonofluoromethane	
2,4,5-Trichlorophenol	196(100), 198(97), 200(31), 97(20)
2,4,6-Trichlorophenol	196(100), 198(96), 200(31), 132(28)
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP or Silvex)	
Trichloropropane, N.O.S.	**
1,2,3,-Trichloropropane	75(100), 39(58), 49(42), 110(37)

MS-ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
O,O,O-Triethyl phosphorothioate	
sym-Trinitrobenzene	
Tris(2,3-dibromopropyl)phosphate	
Vinyl Chloride	62(100), 27(64), 64(33), 26(18)

N.O.S. = not otherwise specified

*Mass spectrum for aldehydes depends upon derivatization method

**Mass spectrum depends on specific compound

APPENDIX A-4
SEMI-VOST SCREENING PROCEDURE

This appendix gives a procedure for screening Appendix VIII compounds for water solubility and organic salt formation, and for estimating compound recovery from acidic-water condensate using the Semi-VOST preparation methodology.

The Semi-VOST procedure used to screen Appendix VIII compounds (POHCs) for their compound interaction with the sample preparation methodology involves the determination of the extent of partitioning of the compounds towards the extraction solvent methylene chloride. The laboratory procedure includes a separatory funnel extraction with methylene chloride to check for the recovery of water-soluble compounds or compounds that form organic salts. The extraction scheme is given in Figure A-4-1. The extraction recovery of the compounds is monitored using UV or HPLC to measure the amount of the compound remaining in the water phase following solvent extraction. An alternate solvent, tertiary-butyl ether, is used to recover extremely water soluble compounds.

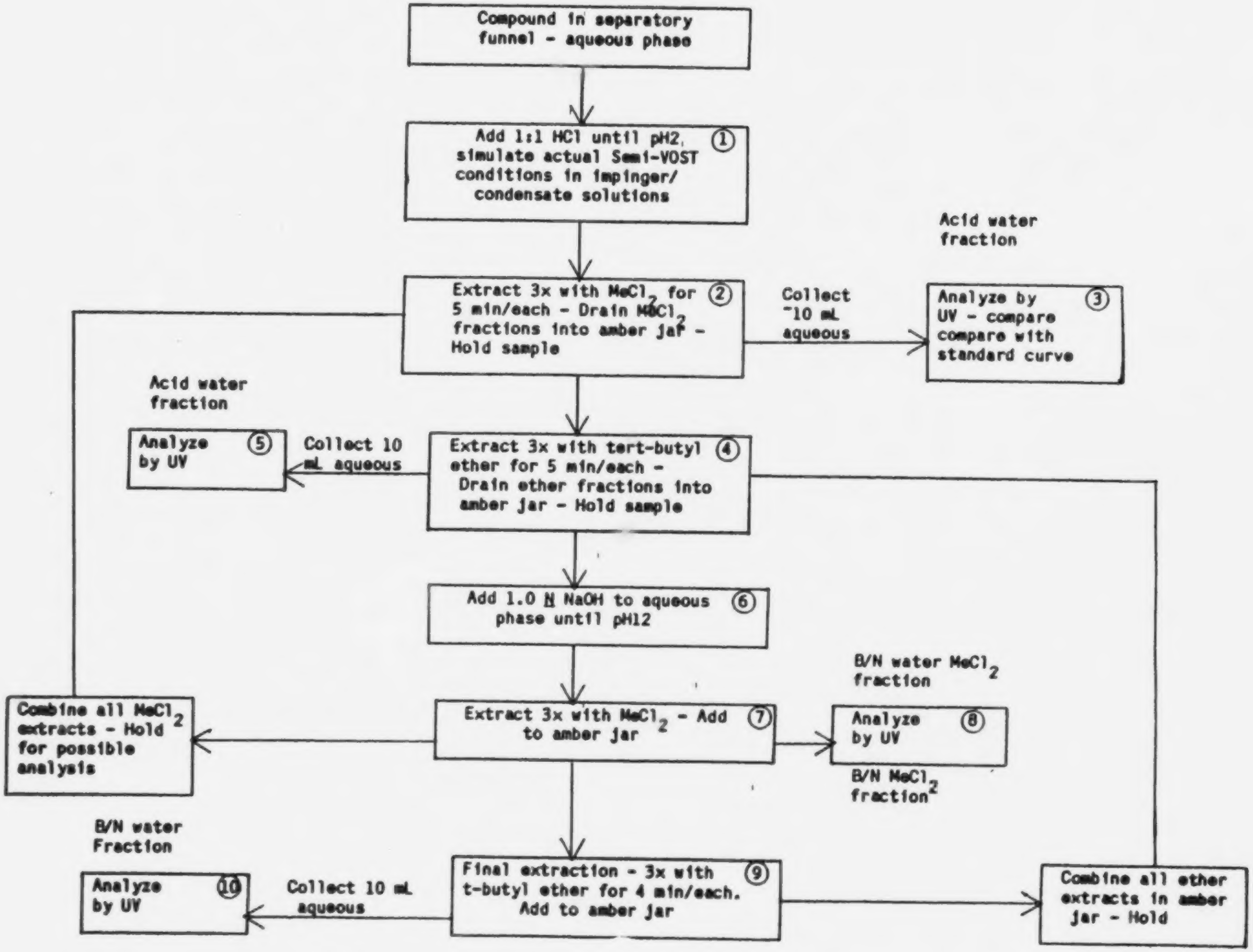

Compound in separatory funnel - aqueous phase
Add 1:1 HCl until pH2, simulate actual Semi-VOST conditions in impinger/ condensate solutions ①
Extract 3x with MeCl2 for 5 min/each - Drain MeCl2 fractions into amber jar - Hold sample ②
Collect ~10 mL aqueous
Acid water fraction
Analyze by UV - compare compare with standard curve ③
Acid water fraction
Analyze by UV ⑤
Collect 10 mL aqueous
Extract 3x with tert-butyl ether for 5 min/each - Drain ether fractions into amber jar - Hold sample ④
Add 1.0 N NaOH to aqueous phase until pH12 ⑥
B/N water MeCl2 fraction
Analyze by UV ⑧
B/N MeCl2 fraction
Combine all MeCl2 extracts - Hold for possible analysis
Extract 3x with MeCl2 - Add to amber jar ⑦
B/N water Fraction
Analyze by UV ⑩
Collect 10 mL aqueous
Final extraction - 3x with t-butyl ether for 4 min/each. Add to amber jar ⑨
Combine all ether extracts in amber jar - Hold

Figure A-4-1. Flowchart for screening Appendix VIII compounds.

APPENDIX B

Precision and Bias

Table 6-7 presented the summary of precision and bias results. A Bartlett test for homogeneity of compound variances produced a chi-square statistic of 20.731 with 4 degrees of freedom. Therefore, the probability was almost zero (P = 0.000) that the compound variances are homogeneous.

The Semi-VOST method precision was expressed in terms of the standard deviation (square root of the variance) and the coefficient of variation of percent recovery. Because the Bartlett test showed the compound variances not to be homogeneous, the standard deviations for all compounds could not be pooled. Therefore, the precision was compound specific.

Table B-1 summarizes the statistics used to test the homogeneity of the run variances of % recovery for each run and the run mean percent recoveries for each spiked compound. The first four columns of numbers pertain to the Bartlett test for homogeneity of run variances, while the last column relates to the ANOVA to test the null hypothesis that the run mean percent recoveries were equal for each compound. Key columns of the table are the final two columns which give the probabilities of making an error if the null hypothesis is accepted. For Bartlett's test the null hypothesis is that the compound variances for all compounds are equal (see Table B-1). For a probability ≤ 0.05, one rejects the null hypothesis and concludes that there is a significant difference in the variances from run to run. But because all of the probabilities for the Bartlett's test are > 0.05 (the level of significance), all the run variances of percent recovery are equal for each compound.

TABLE B-1. STATISTICS FOR RUN VARIANCES AND MEANS

	Statistics for Bartlett's Test[1]				
Compound	B'	F	Degrees of Freedom	Probability	ANOVA Probability
d_5-pyridine	8.987	1.904	4, 130	0.114	0.103
d_8-toluene	7.123	1.999	3, 95	0.119	0.258
d_5-chlorobenzene	3.465	0.942	3, 95	0.423	0.505
d_{10}-o-xylene	3.834	1.046	3, 95	0.376	0.982
d_2-tetrachloro-ethane	4.263	1.167	3, 95	0.326	0.010

[1] B' is the Box modification of the Bartlett test statistic [see Neter, J., W. Wasserman, and Michael H. Kutner," Applied Linear Statistics Models," 2nd ed., Richard D. Irwin, Inc., Homewood, IL 60430 (1985), p. 620].

F is the F statistic for testing the null hypothesis, H_o: $\sigma_1^2 = \sigma_2^2 = \ldots = \sigma^2$.

Degrees of Freedom, e.g., 4, 130 signifies 4 degrees of freedom for runs, 130 is the Box approximation for the degrees of freedom for the denominator of the F statistic.

The ANOVA probabilities indicate that the mean percent recoveries are not equal from run to run for each compound. If 0.05 is chosen as the level of significance, then if the ANOVA probability is ≤ 0.05, the null hypothesis is rejected and a significant difference is indicated. Thus Table B-1 shows that d_2-tetrachloroethane shows a significant mean percent recovery at the 0.01 level of significance. Examination of Table 6-8 showed the mean percent recoveries for Runs 03, 04, 05 and 08 for d_2-tetrachloroethane were 48.8, 97.0, 75.9, and 110.8, respectively. It was probably the mean percent recovery for Run 03, 48.8, that causes the ANOVA probability to be so low. No determinant reason was identified for such a low value. The data was, therefore, retained in the results, and not discarded as an outlier. Note that for the other compounds, no difference in run mean percent recoveries was identified, i.e., the ANOVA probabilities were all greater than 0.05.

Breakthrough Volume

The breakthrough volume results were interpreted with the F test for lack of fit of the data to a linear regression model. Before the breakthrough volume, the amount of deuterated surrogate (ng adsorbed) is related linearly to the sample volume. Beyond the breakthrough volume, the linear relation no longer holds. The F test for lack of fit[3] was used to confirm that the data no longer satisfactorily fit a linear relationship.

Error Sum of Squares. The sum of squares SSE stands for the error sum of squares and is a measure of how well the experimental values of the dependent variable, Y_{ij}, fit the regression relation,

$$\hat{Y}_i = b_1 X_i,$$

where $\hat{Y}_i$ is the calculated value of Y at a given value of X_i, the independent variable. In the case of the distributive volume experiments, X is the sample volume, m^3, and Y is the nanograms of deuterated surrogate compound that adsorbs on the XAD-2® resin.

$$SSE = \Sigma\Sigma (Y_{ij} - \hat{Y}_i)^2 \qquad (1)$$

for the regression model which passes through the origin. The error mean square, or the residual mean square (MSE), is defined in Equation (2).

$$MSE = SSE/(n-1) \tag{2}$$

The error mean square equals the pure error sum of squares (SSPE) plus the lack of fit sum of squares (SSLF), i.e.,

$$SSE = SSPE + SSLF \tag{3}$$

Pure Error Sum of Squares. The sum of squares for pure error assumes that several measurements of Y_{ij} are taken at a given measurement of X_j. Table 6-9 shows that two measurements of Y were taken at $X_j = 1.65$ (1.66 and 1.64), three measurements at $X_j = 5.00$ (5.05, 5.00, and 5.00), and three measurements of Y were taken at $X_j = 10$ (9.98, 10.05, and 10.14).

Thus

$$SSPE = \sum_{j=1}^{c} \sum_{i=1}^{n_j} (Y_{ij} - \overline{Y}_j)^2, \tag{4}$$

where Y_{ij} = an individual measurement of Y at X_j, and

$\overline{Y}_j$ = the average Y_{ij} at X_j.

Pure error mean square, MSPE, is defined in Equation (5).

$$MSPE = SSPE/(n-c), \tag{5}$$

where n = total number of data points, and

c = number of levels of the X variable.

Lack of Fit Sum of Squares. From Equation (3)

$$SSLF = SSE - SSPE, \tag{6}$$

and

$$MSLF = SSLF/(c-1) \tag{7}$$

for the case of regression through the origin.

F test. The appropriate statistic for testing the lack of fit of data to a linear relation is

$$F^* = MSLF/MSPE \tag{8}$$

the critical level of F at a level of significance of α is $F_{1-\alpha, c-1, n-c}$. If F^* is equal to or less than $F_{1-\alpha, c-1, n-c}$, there is not a significant lack of fit. If F^* is greater than $F_{1- , c-1, n-c}$, there is a significant lack of fit.

APPENDIX C
FIELD TEST PROGRAM

Appendix C presents a description of the field testing portion of this program to evaluate the Semi-VOST test method. Included in this appendix are descriptions of the test site and sampling equipment as well as a listing of raw data collected in the field.

C.1 TEST SITE DESCRIPTION

The second Semi-VOST field evaluation was conducted at a facility owned and operated by Smith-Kline Chemicals. An aqueous brine waste stream and spent solvents from the production of fine pharmaceuticals are destroyed at the site in a continuously operated hazardous waste incinerator.

The incinerator, shown schematically in Figure C-1, is a down-fired liquid injection design manufactured by John Zink Company. The incinerator is operated at 12.7 to 15.8 MJ/h (12 to 15 million Btu/h) with a burner temperature of 1815°C (330°F) and a gas temperature of 1010°C (1850°F). Natural gas is burned continuously to support combustion of the aqueous and solvent wastes. A caustic (NaOH) venturi scrubber, operated at a pressure drop of 17.4 to 19.9 kPa (70 to 80 inches of water), is used to control HCl emissions. The scrubber exit gas temperature is approximately 88°C (190°F).

Waste solvent is fed to the incinerator from an agitated 90.9-m^3 (20,000-gallon) storage tank. In an attempt to provide precision estimates for the Semi-VOST method, the waste solvent feed was spiked with chlorobenzene and tetrachloroethylene at a level (approximately 4%) expected to provide detectable quantities of the compounds at the stack outlet.

C.2 SPECIFIED TEST EQUIPMENT

C.2.1 Quad Probe

Semi-VOST field samples were collected using the "quad-probe" sampling system shown in Figure C-2. This system allowed the

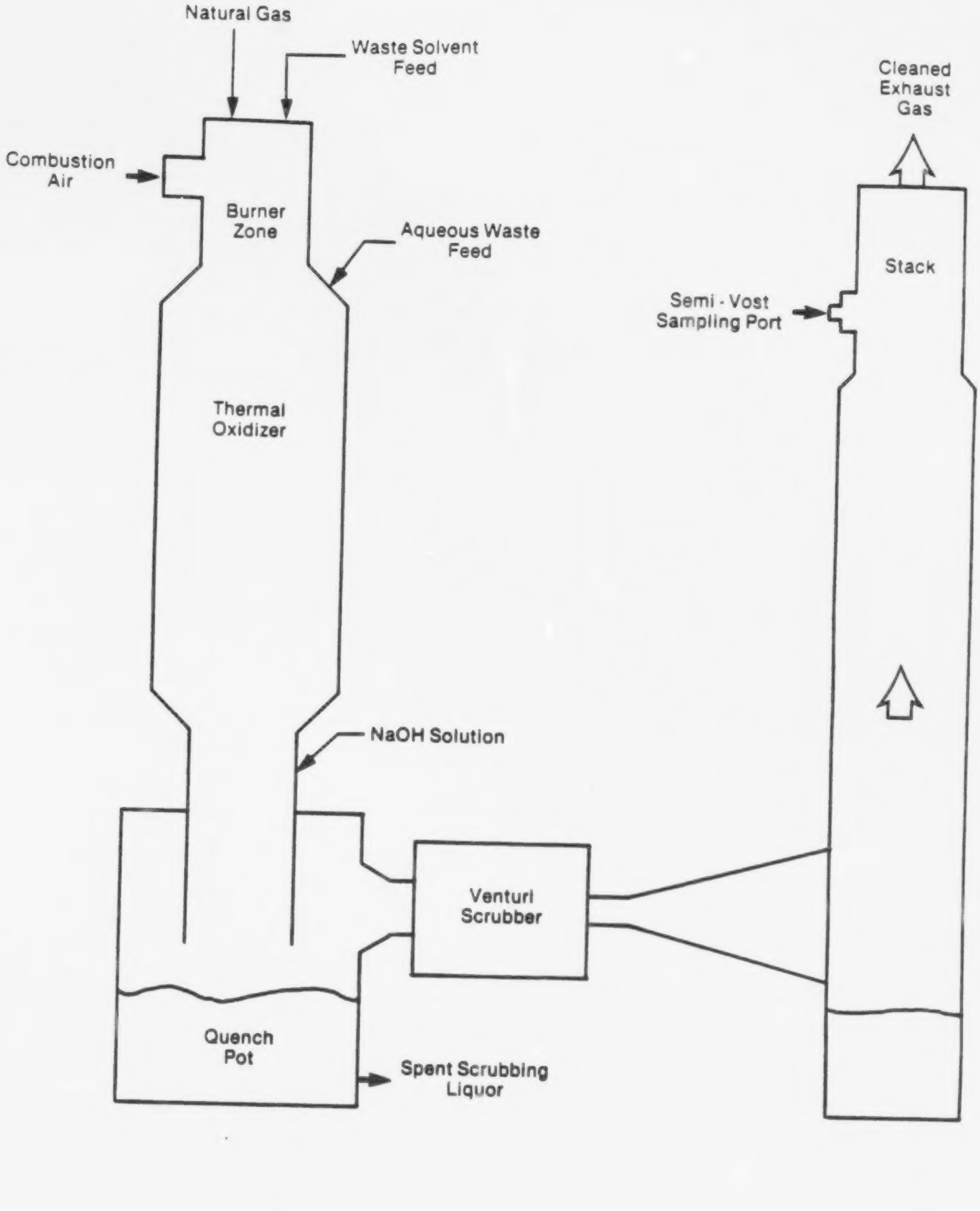

Natural Gas
Waste Solvent Feed
Cleaned Exhaust Gas
Combustion Air
Burner Zone
Aqueous Waste Feed
Stack
Semi - Vost Sampling Port
Thermal Oxidizer
NaOH Solution
Venturi Scrubber
Quench Pot
Spent Scrubbing Liquor

Figure C-1. Diagram of Smith Kline incinerator.

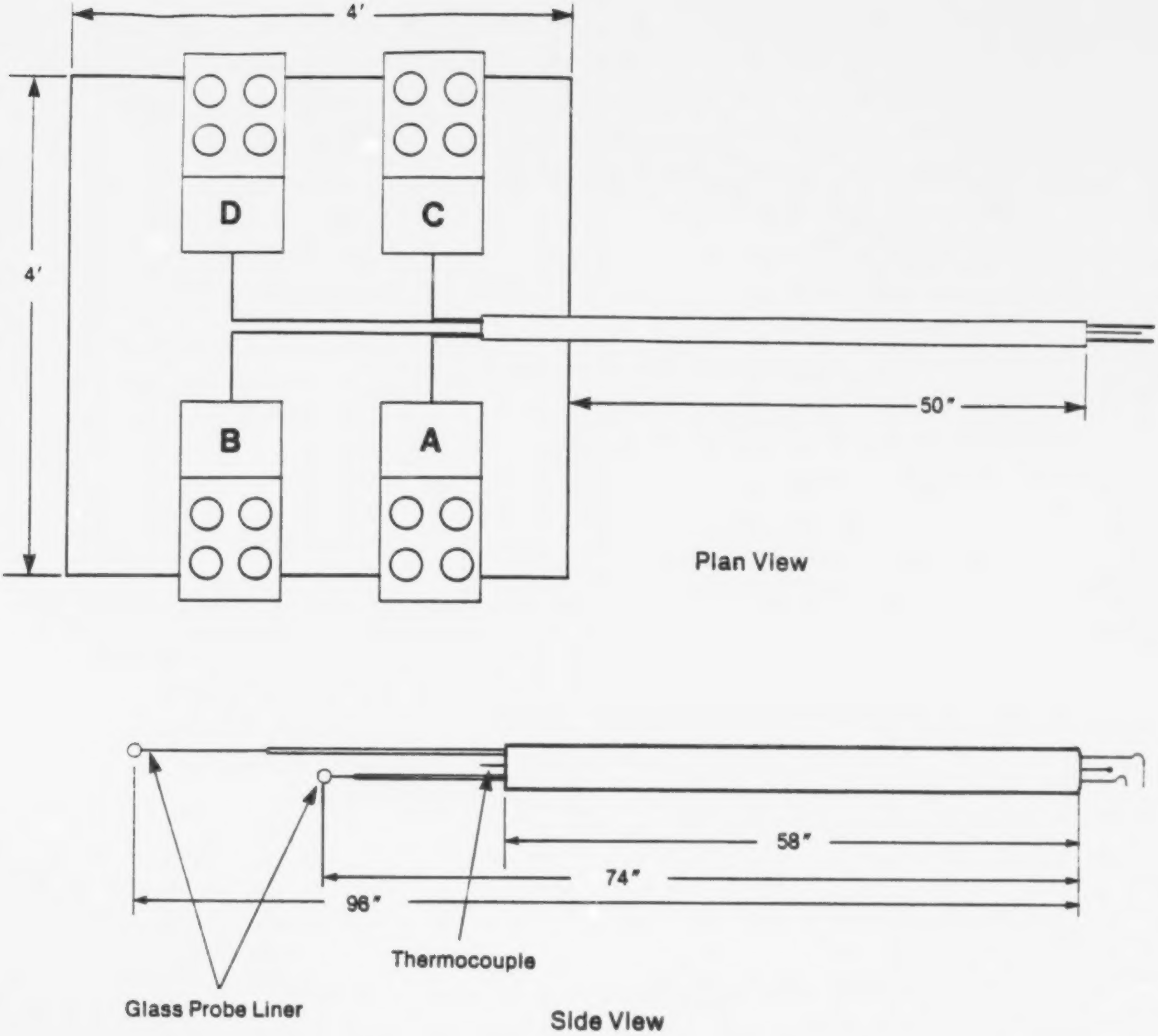
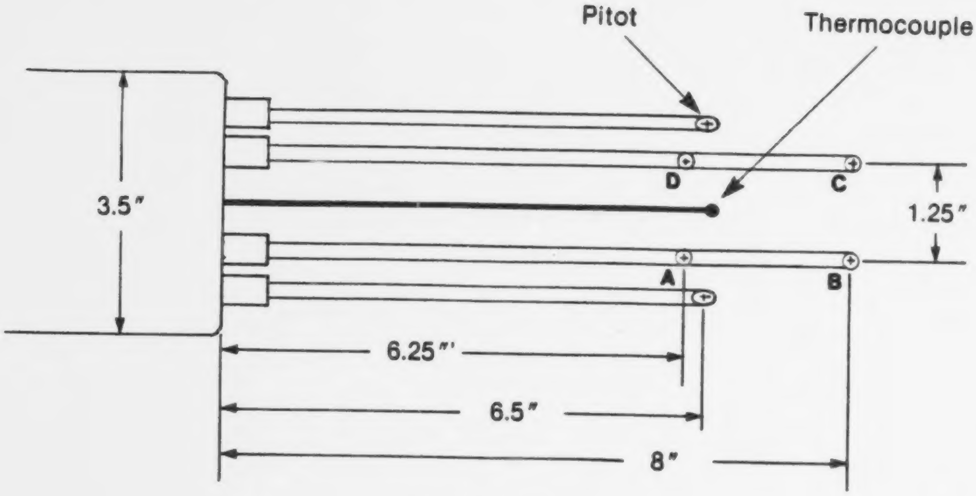

4'
4'
D
C
B
A
50"
Plan View
58"
74"
96"
Thermocouple
Glass Probe Liner
Side View

Figure C-2. Quad train configuration.

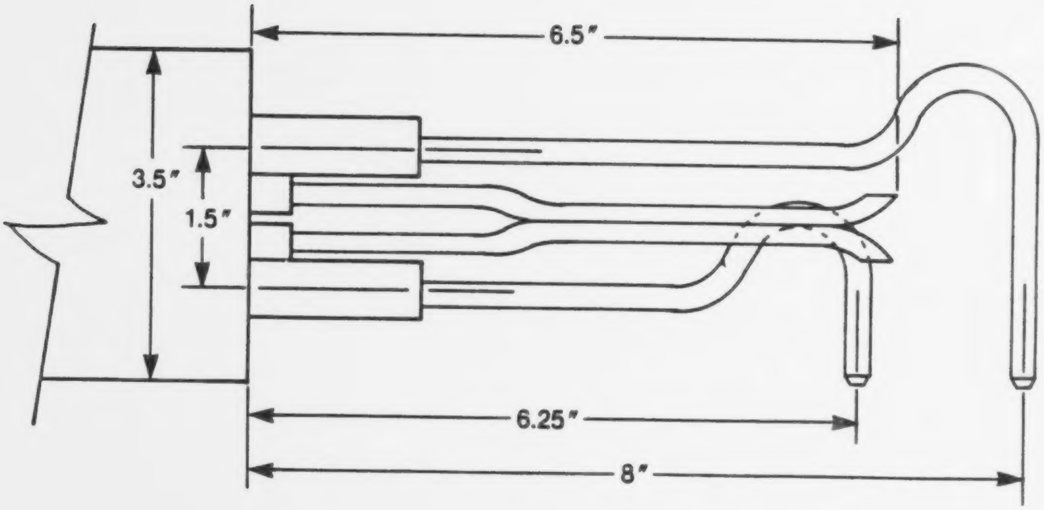
simultaneous collection of four Semi-VOST samples from essentially the same point or location in the stack. The quad-probe assembly consisted of a single probe containing four separate stainless steel probe sheaths, four nozzles, two pitot tubes and one thermocouple. The configuration of the nozzles, pitot tubes and one thermocouple is shown in Figure C-3. Glass probe liners were inserted into the sheaths and connected to the nozzles. The remainder of the sample train from the glass probes back consisted of the standard Semi-VOST train components (filter, condenser, resin trap, etc.) specified in the method formulation (see Appendix A), with one exception. An oversized knockout impinger was inserted into the standard train between the XAD-2® resin trap and the normal knockout impinger.

The oversize impinger offered two advantages. First, using the oversize impinger reduced the frequency that the knockout impinger needed to be emptied during the long retention volume tests. And second, the oversize impinger, as designed, allowed removal of condensate while the train was still drawing flue gas from the stack. The oversize knockout condenser was equipped with a glass siphoning tube that was connected to a length of Teflon® line and a leak tight toggle valve. To empty the knockout impinger, a vacuum was drawn on a "transfer" impinger, a second length of Teflon® line and the toggle valve with a Varistaltic® pump. The toggle valve was then opened and condensate passed through the Teflon® lines to the transfer impinger. Once the transfer was completed, the system was shut down. The contents of the transfer impinger and solvent rinses (acetone, $MeCl_2$) of the transfer system were recovered in labeled sample bottles.

During the Semi-VOST field test, problems with glass probe liner breakage were encountered on the first few test days. The probe liner for Train B was found broken at the end of test run 01 and after 30 minutes of sampling during run 02. The probe liner breakage for Train B was attributed to heat warping of the probe sheath. In order to complete the testing on schedule, two modifications to the original quad-probe system were made. First, all four of the probes were operated at cooler temperatures (near 200°F instead of >250°F), and second a new probe sheath was strapped to the outside of the quad-probe for Train B. The modified nozzle configuration is shown in Figure C-4.


Pitot
Thermocouple
3.5″
D
C
1.25″
A
B
6.25″
6.5″
8″

Bottom View


6.5″
3.5″
1.5″
6.25″
8″

Side View

Figure C-3. Quad probe sampling nozzle configuration.

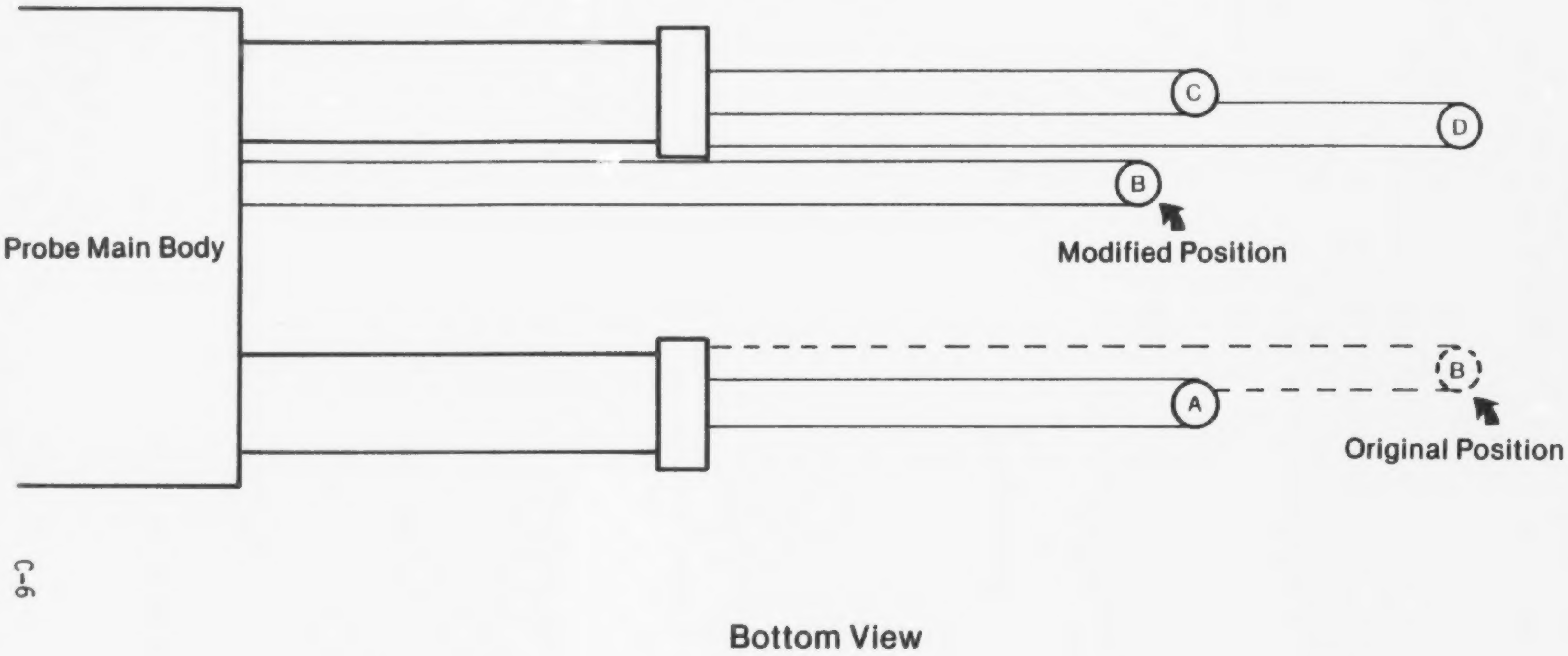

Probe Main Body
C
D
B
Modified Position
A
B
Original Position
Bottom View

Figure C-4. Modified quad probe nozzle configuration.

The Semi-VOST samples were collected at a point of average velocity, approximately 0.46 m (18 inches) into the stack. The sample trains were generally operated to obtain the desired sampling rate of 0.5 cfm instead of operating to maintain an isokinetic sampling rate.

C.3 Dynamic Spiking System

The dynamic spiking of the sampling trains with d_8-toluene, d_5-chlorobenzene, d_2-1,1,2,2-tetrachloroethane, d_5-pyridine and d_{10}-*o*-xylene was accomplished utilizing the apparatus shown in Figure 6-3. Specific components of the dynamic spiking system included separate pressure regulators and precision flow controllers for each sample train, a heat lamp, circulating fan, and a temperature controller to maintain constant temperature in the control box. A multichannel flow controller readout for monitoring the flow was also included.

Two identical spiking systems were used - one for Trains A and B and one for Trains C and D. Each spiking system was fed by a low-pressure compressed gas cylinder containing a mixture of the five deuterated spiking compounds, balanced in high purity nitrogen, at a compound concentration of 100 MDL.

Cylinders containing the deuterated compounds were order from Scott Specialty Gases and analyzed in the laboratory before and after the field test. The analytical results are given in Table C-1. A standard curve was prepared using 1 uL injections of standard solutions prepared using the non-deuterated homologs of the compounds. A known volume of gas from each cylinder was injected into the gas chromatograph using a gas sampling loop. The concentration of the gas in the cylinder was then calculated using the prepared curve, a conversion factor to convert mg/m^3 to ppm, and the average area counts of the sample.

Before going to the field, the measured concentration of each component in cylinders was found to be within 12 percent of the manufacturer's reported values with the exception of d_2-1,1,2,2-tetrachloroethane in cylinder #11584. Cylinders #4295 and #14945 were purchased while in the field and were not analyzed before the test. After returning from the field, the measured concentrations

Table C-1. ANALYSIS OF CYLINDERS CONTAINING DEUTERATED SPIKE GAS

Cylinder No.	Compound	Scott Concentration (ppm)	May Measured Concentration (ppm)	May Percent Difference	July Measured Concentration (ppm)	July Percent Difference
4295	d_5-pyridine	547.8	---	---	523.8	-4.38
	d_2-tetrachloroethane	6.668			7.188	7.80
	d_8-toluene	105.9			103.3	-2.46
	d_5-chlorobenzene	16.75			16.91	0.96
	d_{10}-o-xylene	96.20			93.23	-3.09
4585	d_5-pyridine	547.2	535.4	-2.15	---	---
	d_2-tetrachloroethane	7.36	7.038	-4.38	---	---
	d_8-toluene	105.6	97.28	-7.88	---	---
	d_5-chlorobenzene	17.25	16.41	-4.86	---	---
	d_{10}-o-xylene	97.09	95.49	-1.65	---	---
6923	d_5-pyridine	546.4	486.8	-10.9	---	---
	d_2-tetrachloroethane	7.867	7.167	-8.89	---	---
	d_8-toluene	107.9	97.79	-9.37	---	---
	d_5-chlorobenzene	19.89	17.59	-11.57	---	---
	d_{10}-o-xylene	97.2	89.40	-8.03	---	---

$$\text{Percent Difference} = \frac{\text{measured value} - \text{reference value}}{\text{reference value}} \times 100$$

Table C-1. Continued

Cylinder No.	Compound	Scott Concentration (ppm)	May Measured Concentration (ppm)	May Percent Difference	July Measured Concentration (ppm)	July Percent Difference
9188	d_5-pyridine	592.8	566.2	-4.50	537.1	-9.40
	d_2-tetrachloroethane	8.034	7.738	-3.68	7.597	-5.44
	d_8-toluene	108.6	112.2	3.28	106.8	-1.69
	d_5-chlorobenzene	19.28	19.36	0.41	19.40	0.62
	d_{10}-o-xylene	100.3	107.3	6.94	99.52	-0.78
11584	d_5-pyridine	586.6	643.4	9.68	---	---
	d_2-tetrachloroethane	5.66	3.956	-30.10	---	---
	d_8-toluene	110.5	107.9	-2.38	---	---
	d_5-chlorobenzene	19.73	19.56	-0.84	---	---
	d_{10}-o-xylene	99.17	106.8	7.71	---	---
14945	d_5-pyridine	547.1	---	---	504.4	-7.80
	d_2-tetrachloroethane	6.901	---	---	6.764	-1.98
	d_8-toluene	106.5	---	---	101.8	-4.40
	d_5-chlorobenzene	16.95	---	---	17.07	0.73
	d_{10}-o-xylene	96.55			88.99	-7.83
16527	d_5-pyridine	548.5	600.5	9.48	523.5	-4.56
	d_2-tetrachloroethane	6.758	6.546	-3.13	6.198	-8.29
	d_8-toluene	108.0	102.9	-4.76	107.2	-0.77
	d_5-chlorobenzene	16.62	16.55	-0.43	17.59	5.85
	d_{10}-o-xylene	97.69	98.60	0.93	97.56	-0.13
16580	d_5-pyridine	547.9	590.0	7.68	493.4	-9.95
	d_2-tetrachloroethane	6.313	5.697	-9.76	5.438	-13.86
	d_8-toluene	106.1	99.56	-6.16	97.72	-7.90
	d_5-chlorobenzene	17.09	16.30	-4.60	16.54	-3.20
	d_{10}-o-xylene	97.4	96.16	-1.28	90.18	-7.41

of all components in all cylinders were within 10 percent of the reported Scott values with the exception of d_2-1,1,2,2-tetrachloroethane in cylinder #16580. Cylinders #4585 and #6923 were not used in the field and were not analyzed after the field trip.

Although the cylinders were ordered at different times, the same deuterated compounds were used to prepare all of the cylinders. Samples from two of the cylinders were analyzed by mass spectroscopy. No undeuterated homologs of the compounds of interest were found.

The flow controllers on the dynamic spiking system were set to deliver 20 cc/min each to Trains A, B, C and D during Runs 1-5, to Trains A, B and C during Runs 6, 7, and 10 and to Trains A and B during Runs 8 and 9. The gaseous spike entered each train through a glass "T" located after the filter and before the condenser of each train.

Unheated, uninsulated, 1/4-inch Teflon® lines connected the gas cylinders to the flow controllers. The flow controllers were housed in a heated environment at approximately 90°F (32°C). One-eighth inch Teflon® lines, sheathed in 1/4-inch Teflon® and foam insulation connected the flow controllers to the Semi-VOST sampling trains. A three-way valve was placed before the sampling train so that flow from the dynamic spiking system could be directed either to the sampling train or to exhaust.

For proper operation, each flow controller required a minimum pressure drop of 1.4 Kg/cm^2 (20 psig). The pressure exiting the gas cylinders was maintained at 2.8 Kg/cm^2 (40 psig).

The spiking system described above was calibrated and tested in the laboratory prior to this field testing. The flow controllers were calibrated under operating conditions. The standard operating procedure and calibration data for Channels 1 through 4 are presented in Appendix C.1. Channel 1 was used to spike Train A; Channel 2 to spike Train B; Channel 3 to spike Train C and Channel 4 to spike Train D.

The results of the preliminary laboratory tests showed that the spiking system required a finite equilibration time before accurate compound delivery could be expected. The optimal time was found to be approximately 2 hours. The minimum equilibration time allowed during these tests was 2 hours.

Throughout each run the dynamic spiking system was periodically monitored. A soap film flow meter was used to check the flows of the mass flow controllers prior to testing, during breaks in the testing and at the completion of the testing. At the end of each test day, a mean flow rate, standard deviation and relative standard deviation were calculated for each train. The results are reported in Table C-2. Except for Train B, Run 6 which varied by 6.1 percent, the flows varied by less than 3 percent throughout each test.

Plots showing the stability of the measured flow rate coming out of the dynamic spiking system and directed to each train are shown in Figures C-5 to C-8. The x-axis is in clock hours where values less than 12 indicate morning measurements, values between 12 and 24 indicate afternoon measurements, and values 24 and greater indicate measurements taken after midnight. The y-axis is in mL/min and is an expanded scale to magnify the observed variances in the measured flows.

Samples of the spiking gas were obtained from each train at the beginning and completion of each test. The samples were collected with the three-way valve set to exhaust. For each train a 50-mL gas-tight syringe was used to draw-up the sample. To insure that a vacuum was not created and that dilution of the sample did not occur, the sample was withdrawn through a T-connector with a water bubbler attached at one end. The presence of bubbles indicated that excess sample was passing the sampling point verifying that the obtained sample was representative.

The samples were analyzed by GC/FID to verify the concentrations of each of the five spiking components. Chromatographic conditions are listed in Table C-3. A cylinder of the five-component mix was used as a reference and a quality control (QC) standard to verify the stability of the FID. At the end of each test day, a mean area count, standard deviation and relative standard deviation were calculated for each component of the QC standard. The data is shown in Table C-4.

After Run 2 (which was aborted), the sensitivity of the FID was increased so that the tetrachloroethane concentration could be measured.

Table C-2. DYNAMIC SPIKING SYSTEM MONITORING: FLOW RATES

Run No.	Date	Train	Mean Flow Rate (mL/min)	Standard Deviation	Coefficient of Variation
1	06/17/86	A	19.40	0.35	1.80
		B	19.66	0.17	0.87
		C	19.35	0.13	0.68
		D	19.47	0.11	0.59
3	06/19/86	A	19.10	0.48	2.51
		B	19.84	0.31	1.58
		C	19.62	0.21	1.08
		D	19.40	0.43	2.23
4 & 5	06/20/86	A	19.84	0.23	1.18
		B	20.01	0.18	0.89
		C	20.06	0.29	1.43
		D	19.67	0.09	0.44
6	06/23/86	A	20.61	0.24	1.18
		B	21.16	1.29	6.11
		C	20.67	0.25	1.23
7 (Day 1)	06/24/86	A	20.04	0.23	1.14
		B	20.34	0.46	2.28
		C	20.10	0.19	0.94
7 (Day 2)	06/25/86	A	19.53	0.13	0.68
		B	19.39	0.05	0.27
		C	19.55	0.18	0.93
8 & 9	06/26/86	A	19.83	0.19	0.94
		B	19.68	0.20	1.00
10	06/27/86	A	20.74	0.05	0.22
		B	20.32	0.35	1.72
		C	20.65	0.12	0.58

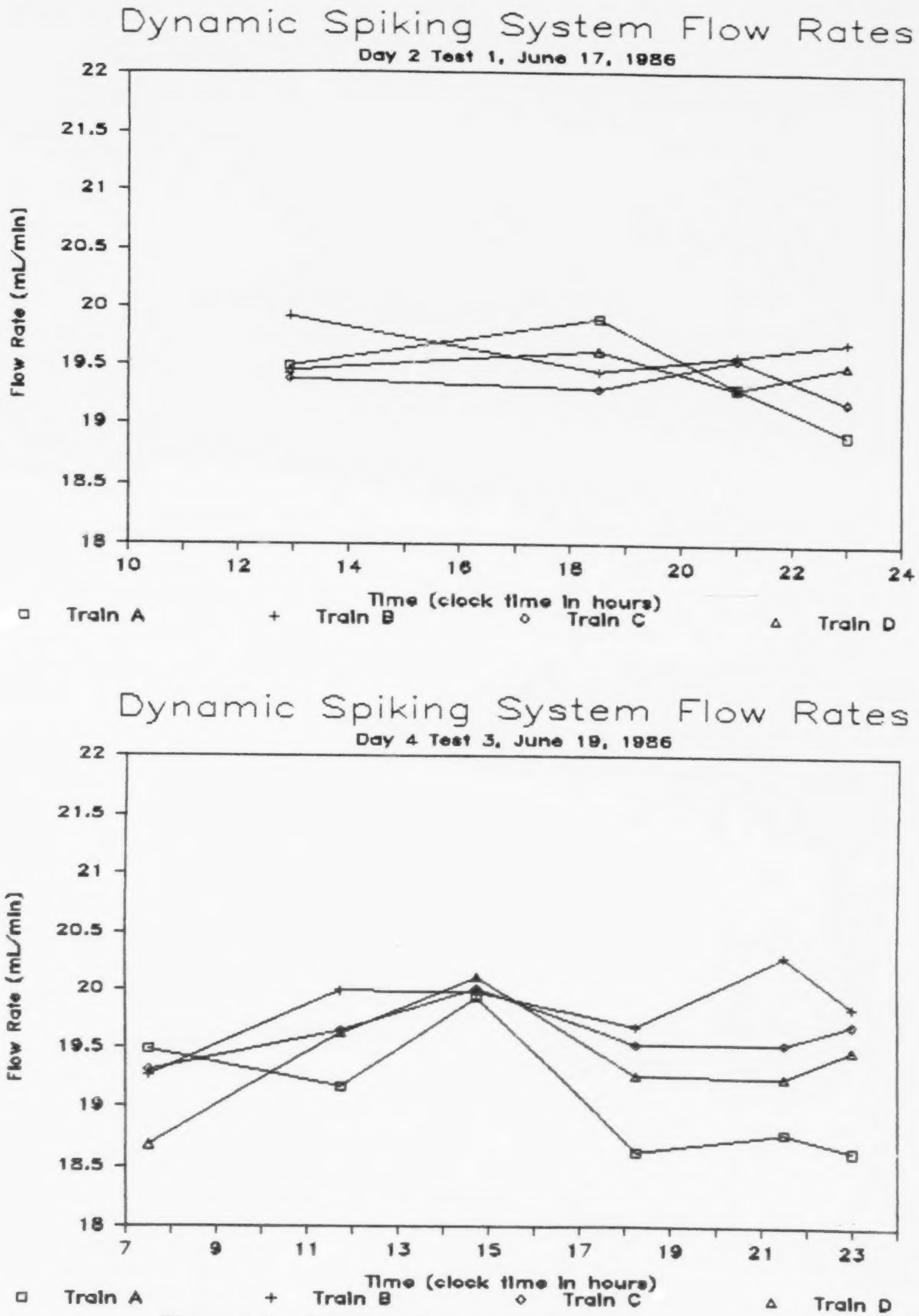


Figure C-5. Measured flow rates vs. time.

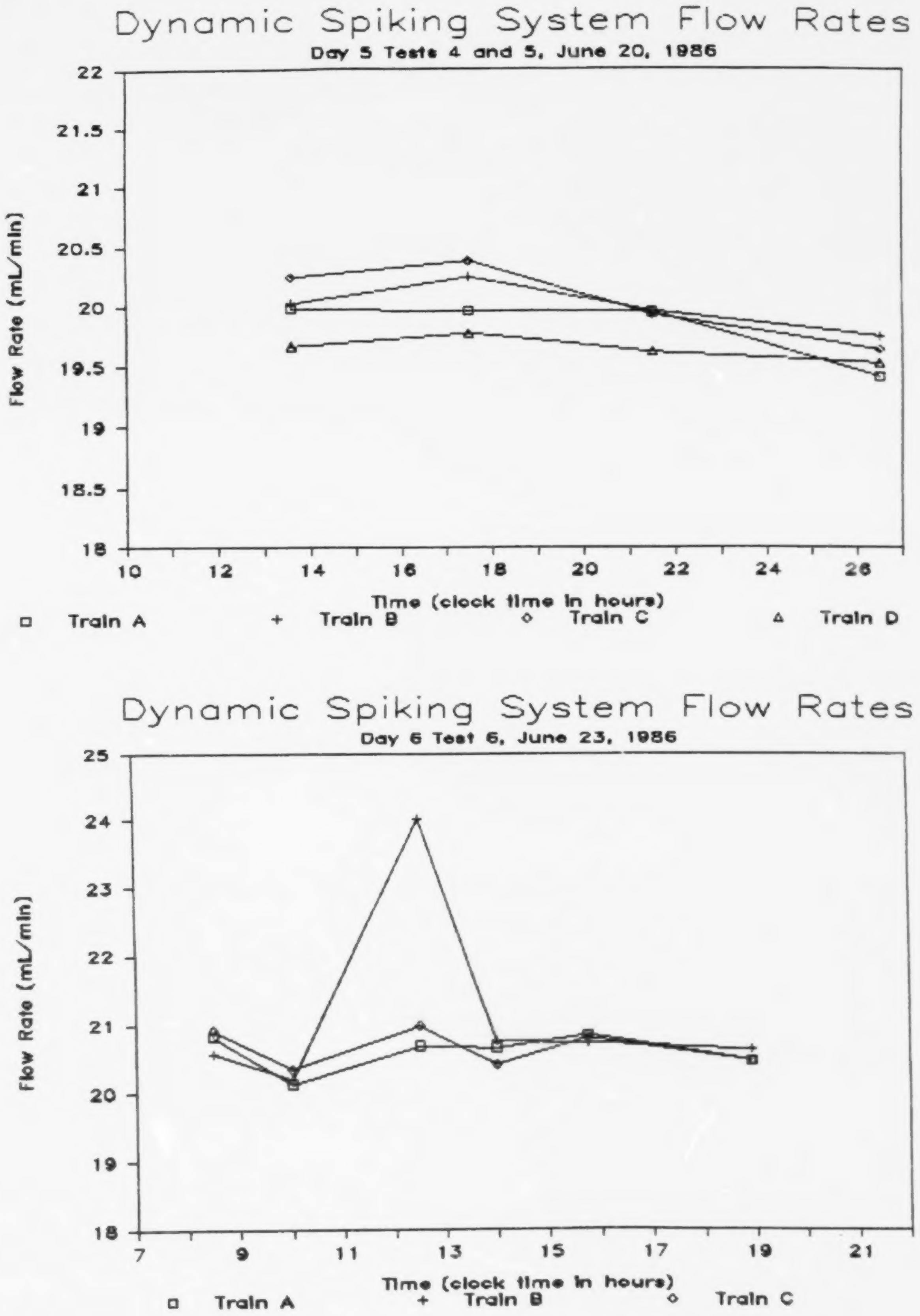
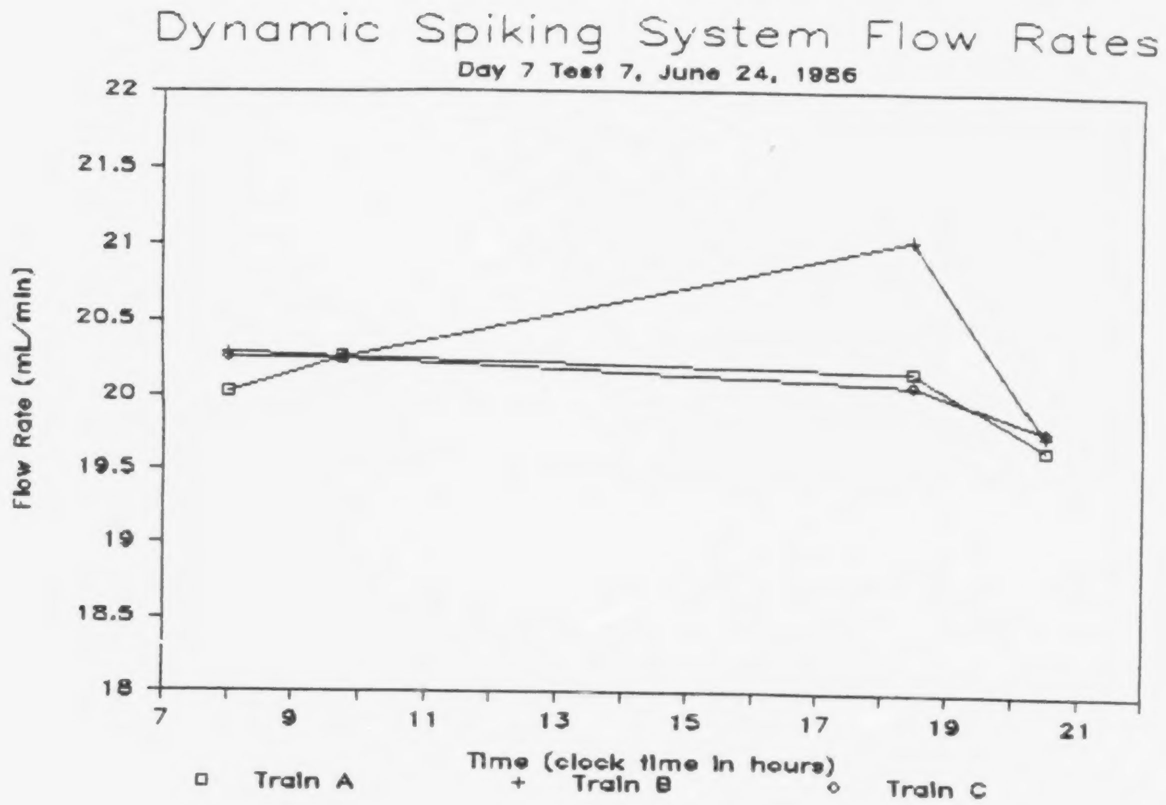
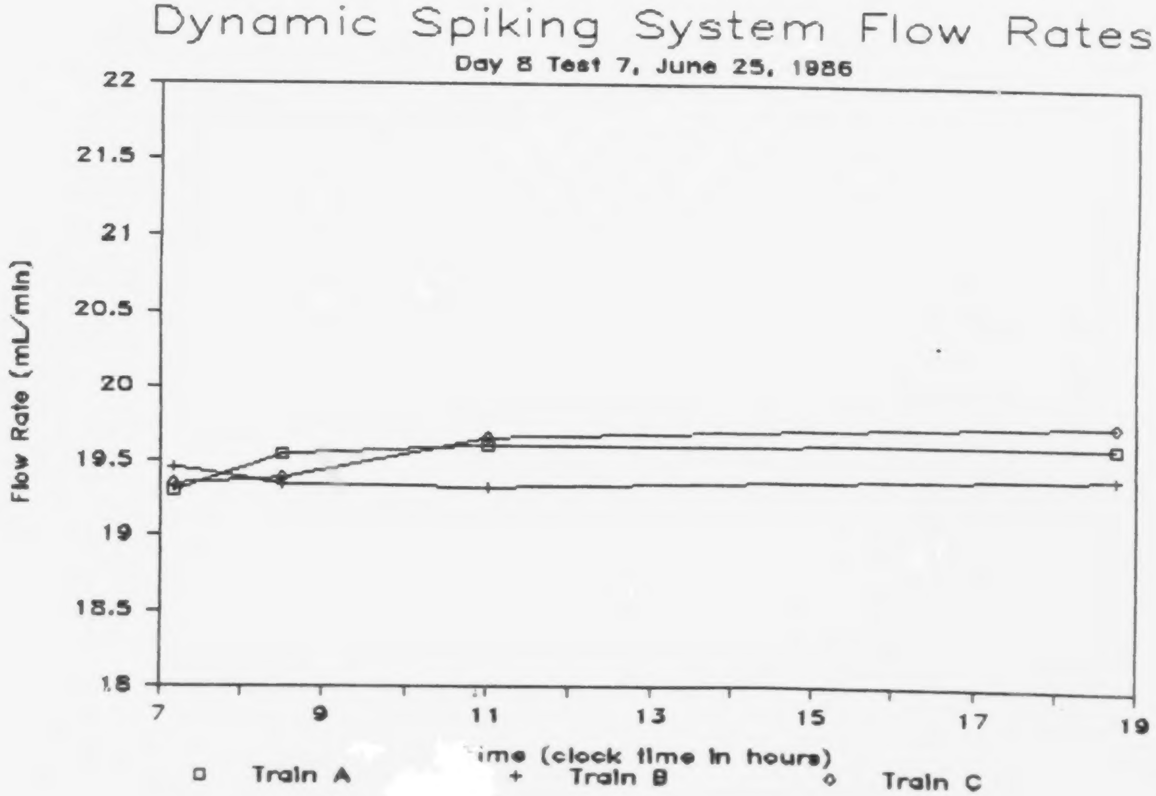
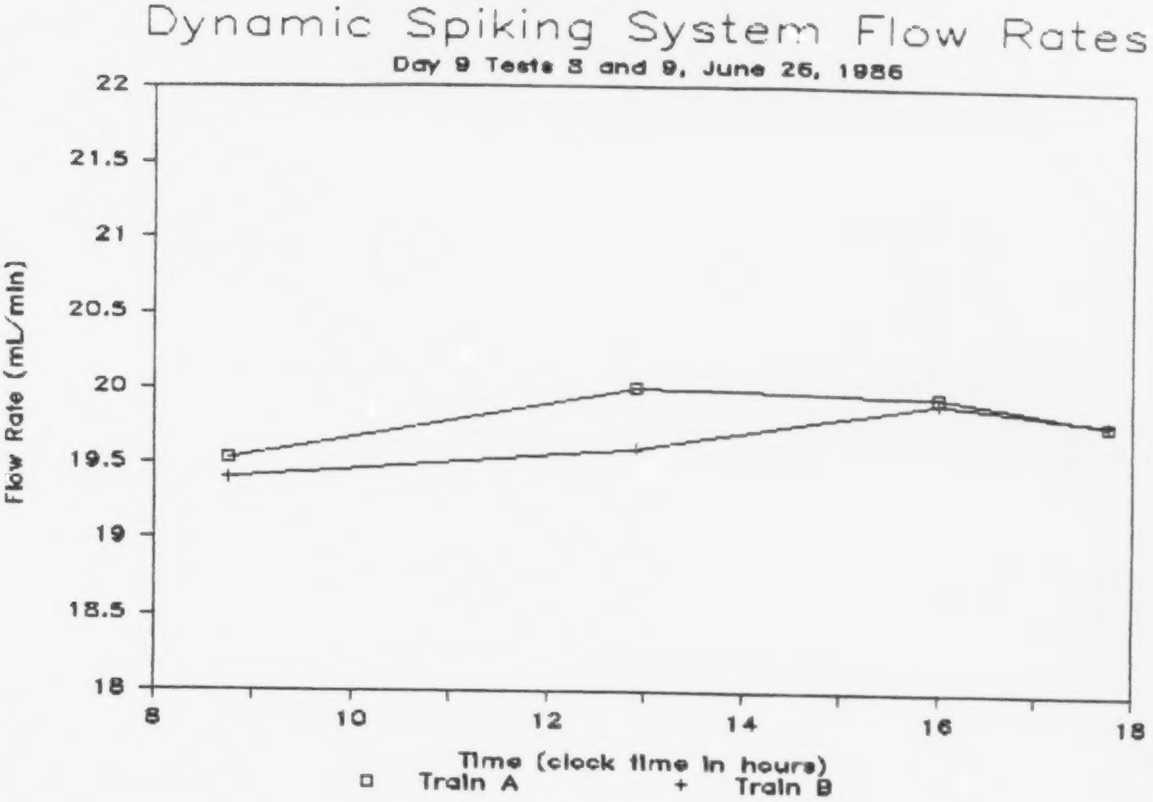


Figure C-6. Measured flow rates vs. time.

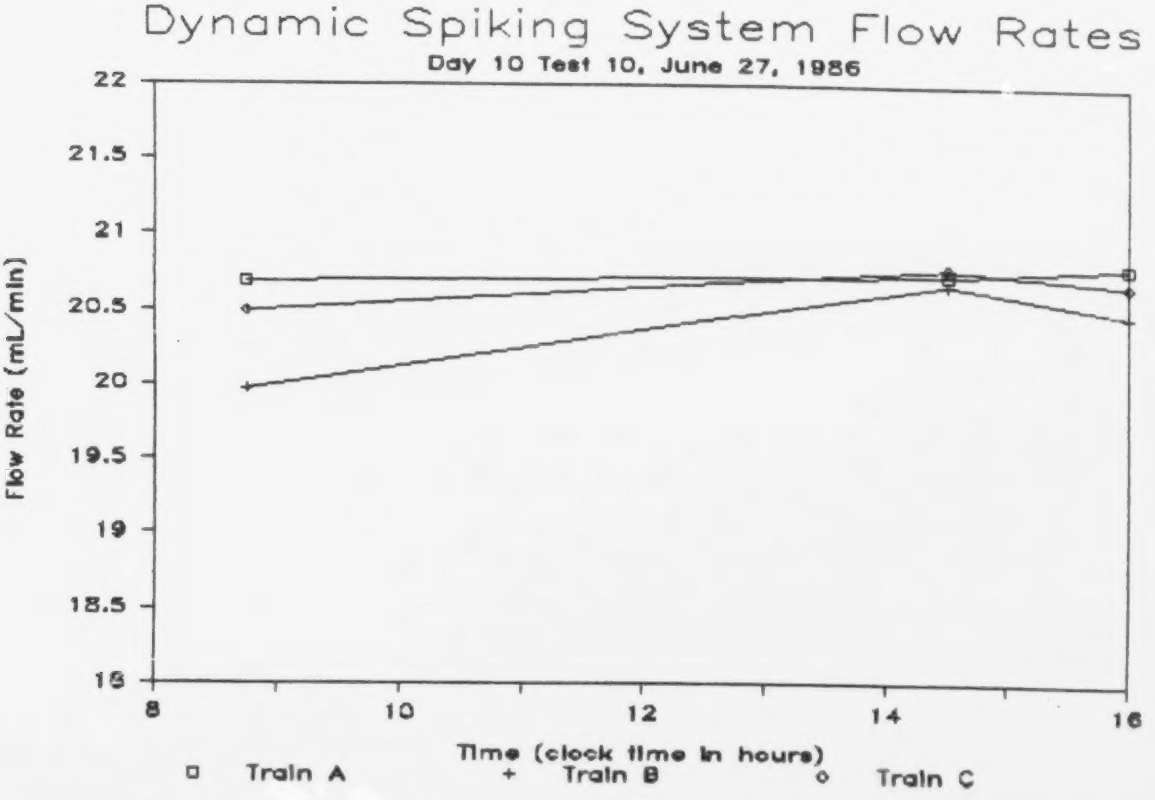




Figu[illegible]. Measured flow rates vs. time.


Dynamic Spiking System Flow Rates

Day 9 Tests 8 and 9, June 26, 1986


Dynamic Spiking System Flow Rates

Day 10 Test 10, June 27, 1986

Figure C-8. Measured flow rates vs. time.

TABLE C-3. GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Varian 3400 w/IBDH and/or Shimadzu recorder/integrator

Detector: Flame Ionization at 300 °C

- Hydrogen Flow: 30 cc/min.
- Air Flow: 300 cc/min.

Column: 1% SP-1000 on 60/80 mesh Carbopack B, 6 ft. × 1/8 in., stainless steel

- Program:
  - Initial Temperature: 150 °C, no hold
    - Ramp Rate: 16 °C/min.
  - Second Temperature: 220 °C, hold 6 min.
    - Ramp Rate: 16 °C/min.
  - Final Temperature: 250 °C, hold 2 min.

Carrier: Nitrogen at 30 cc/min.

Injector Port Temperature: 250 °C

Sample Introduction: Valve

Table C-4. GAS CHROMATOGRAPHIC STABILITY

Run No.	Date	Compound	Mean Area Count	Standard Deviation	Relative Standard Deviation
1	86/06/17	d_5-pyridine	1,219,812	55,581	4.56%
		d_2-tetrachloroethane	1,370	---	---
		d_8-toluene	385,995	22,976	5.95%
		d_5-chlorobenzene	54,659	3,212	5.88%
		d_{10}-o-xylene	421,828	27,578	6.54%
3	86/06/19	d_5-pyridine	37,894,953	14,741,657	38.90%
		d_2-tetrachloroethane	59,609	22,885	38.39%
		d_8-toluene	10,784,236	3,311,051	30.70%
		d_5-chlorobenzene	1,770,553	689,848	38.96%
		d_{10}-o-xylene	14,406,227	6,013,893	41.75%
4 & 5	86/06/20	d_5-pyridine	21,260,934	615,238	2.89%
		d_2-tetrachloroethane	96,836	11,379	11.75%
		d_8-toluene	6,218,386	63,330	1.02%
		d_5-chlorobenzene	892,892	26,516	2.97%
		d_{10}-o-xylene	7,867,605	219,712	2.79%
6	86/06/23	d_5-pyridine	23,458,264	660,493	2.82%
		d_2-tetrachloroethane	121,046	6,153	5.08%
		d_8-toluene	6,952,337	91,908	1.32%
		d_5-chlorobenzene	1,016,062	29,062	2.86%
		d_{10}-o-xylene	8,370,829	191,903	2.29%

Table C-4. Continued

Run No.	Date	Compound	Mean Area Count	Standard Deviation	Relative Standard Deviation
7 (Day 1)	86/06/24	d_5-pyridine	21,533,529	1,996,850	9.27%
		d_2-tetrachloroethane	98,399	16,412	16.68%
		d_8-toluene	6,757,966	333,915	4.94%
		d_5-chlorobenzene	947,410	60,488	6.38%
		d_{10}-o-xylene	8,065,560	712,855	8.84%
7 (Day 2)	86/06/25	d_5-pyridine	21,174,041	670,374	3.17%
		d_2-tetrachloroethane	119,964	12,005	10.01%
		d_8-toluene	6,553,172	228,385	3.49%
		d_5-chlorobenzene	946,372	34,466	3.64%
		d_{10}-o-xylene	8,232,406	397,469	4.83%
8 & 9	86/06/26	d_5-pyridine	22,339,700	991,610	4.44%
		d_2-tetrachloroethane	123,667	8,273	6.69%
		d_8-toluene	6,939,632	105,446	1.52%
		d_5-chlorobenzene	1,014,121	28,168	2.78%
		d_{10}-o-xylene	8,432,134	235,885	2.80%
10	86/06/27	d_5-pyridine	23,484,591	1,113,914	4.74%
		d_2-tetrachloroethane	127,172	3,673	2.89%
		d_8-toluene	7,124,640	126,083	1.77%
		d_5-chlorobenzene	1,041,605	32,275	3.10%
		d_{10}-o-xylene	8,566,149	59,512	0.69%

On June 19 (Run 3) the FID on the GC would not light because of a bad hydrogen needle valve. While trouble-shooting the GC, the heated valve was turned off and never turned back on. The large intraday variance (30-50 percent) is due to the different volume of sample injected as the valve cooled.

For d_5-pyridine, d_8-toluene, d_5-chlorobenzene and d_{10}-o-xylene the signal varied less than 6 percent from day to day for Runs 4 through 10 (June 20-27). Throughout the day for these four compounds the signal varied less than 10 percent during every run but Run 3 (June 19). For the tetrachloroethane the FID signal varied by 12 percent from day to day and by up to 17 percent throughout the day. This larger variance in the tetrachloroethane signal is attributed to two facts:

(1) the tetrachloroethane is present in low quantities (less than 10 ppm), and

(2) the tailing of the earlier eluting pyridine interferes with the tetrachloroethane.

This data is also presented in Figures C-9 to C-16. Data for each day is on a separate page. The x-axis is in clock hours and the y-axis of the top plot is in raw area counts and of the bottom plot is in adjusted area counts. The adjusted area counts were obtained by dividing the area counts for a given component by an arbitrary factor. The arbitrary factor was chosen to enable all five components to be plotted on one graph with equal detail.

The concentration for a given component was calculated by direct comparison of the area counts of the sample to the area counts of the quality control cylinder. An average daily response factor for each component of the QC cylinder was calculated by averaging the area counts obtained for that component on that day and dividing by the concentration measured by Scott Specialty Gases. The average area counts for that component in the spiking gas was then divided by the average daily response factor to give an average spike gas concentration for that component on that day. This data is presented in Table C-5. These concentration values were used to calculate the ration of measured concentration to expected concentration (Table 6-1) and the amount of material actually spiked onto the XAD-2® resin (Table C-6).

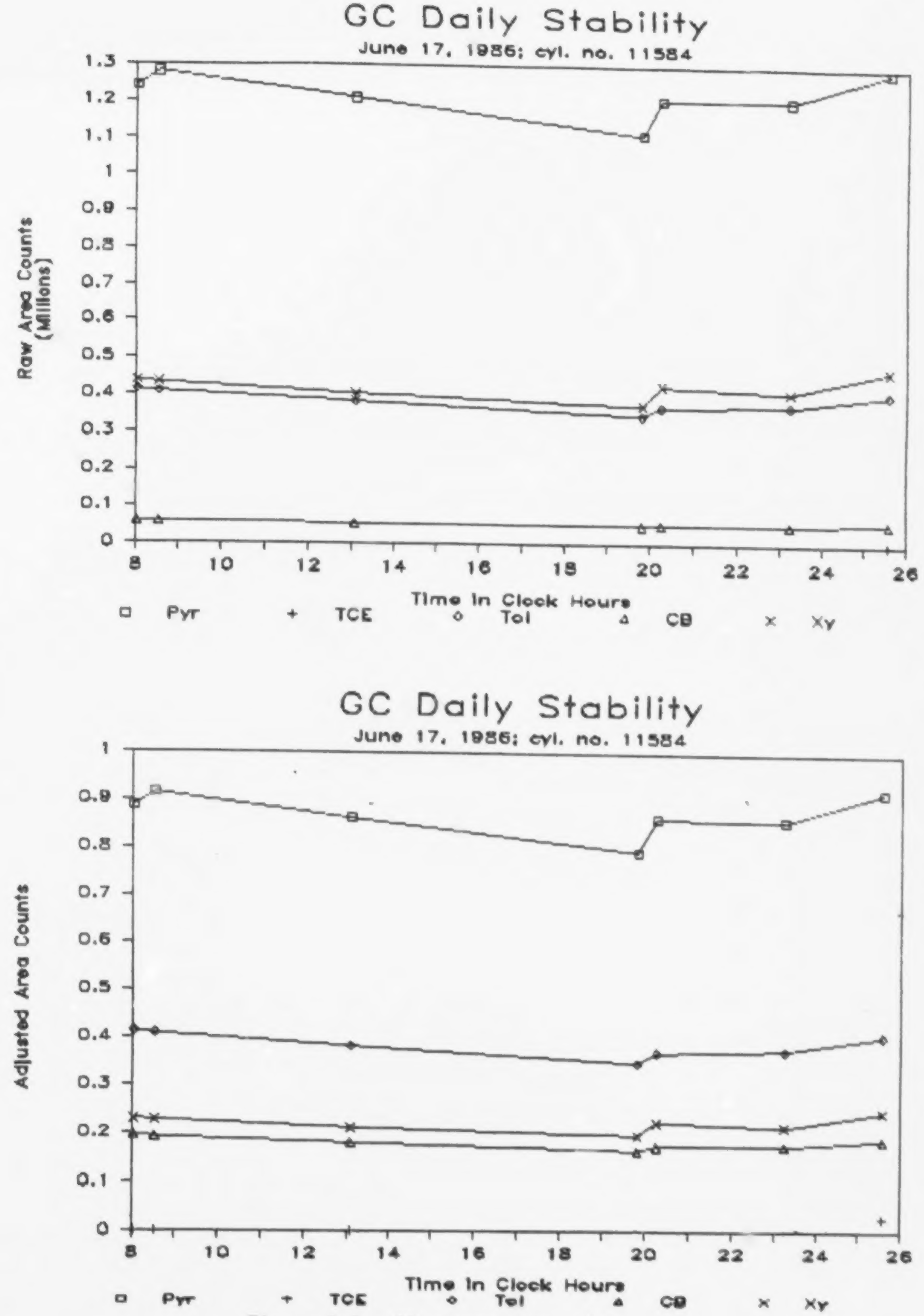


Figure C-9. GC response vs. time.

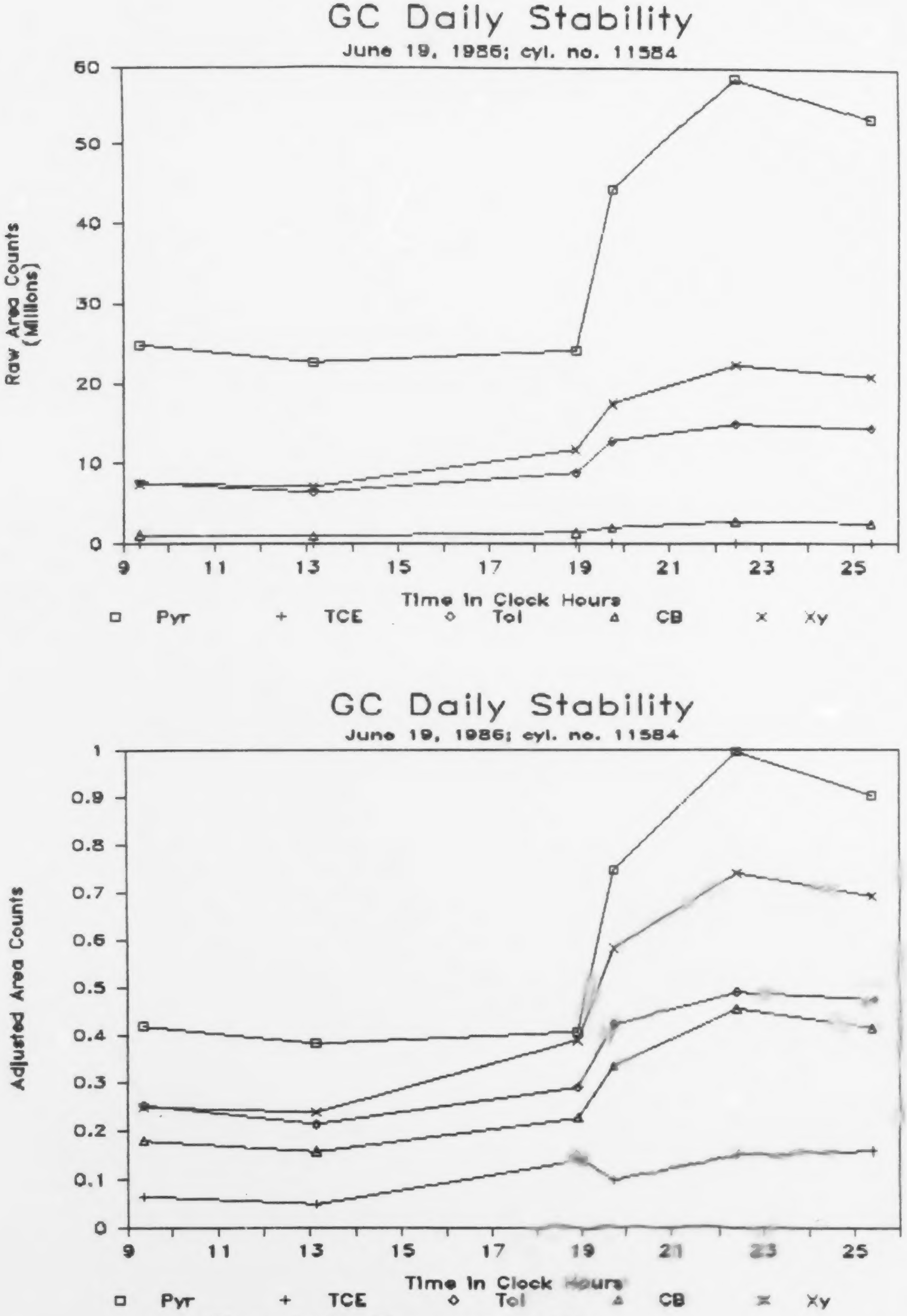


Figure C-10. GC response vs. time.

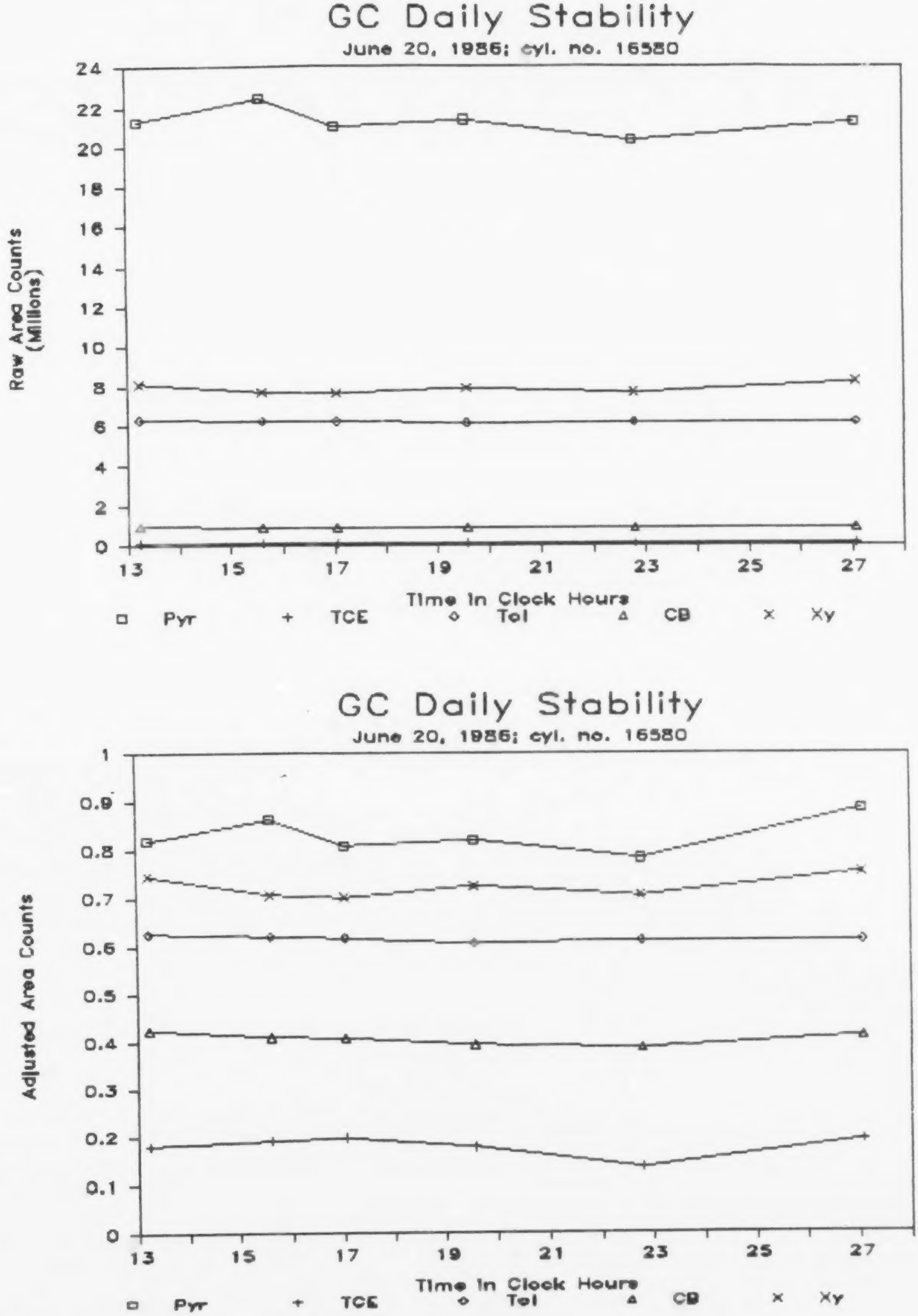


Figure C-11. GC response vs. time.

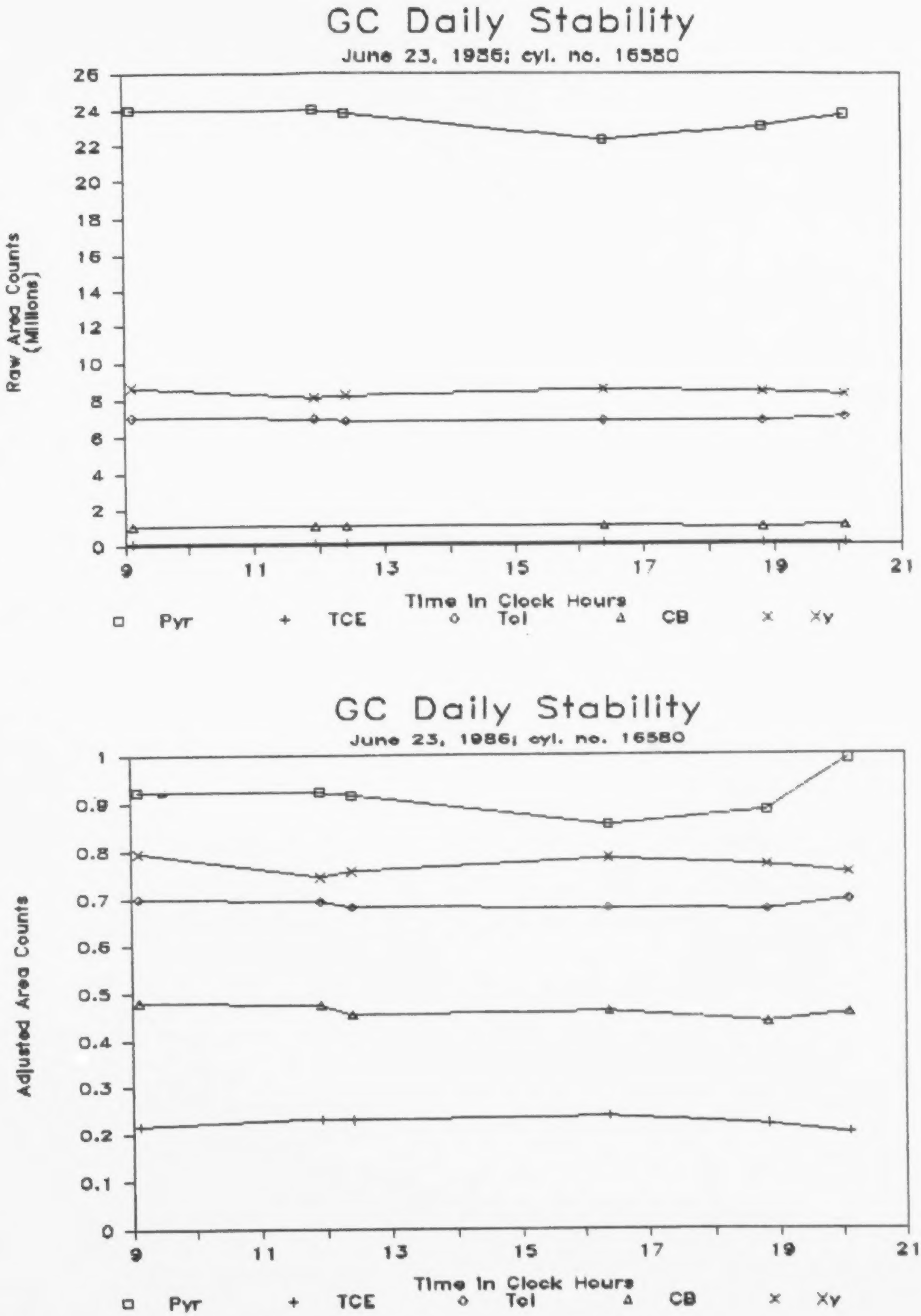


Figure C-12. GC response vs. time.

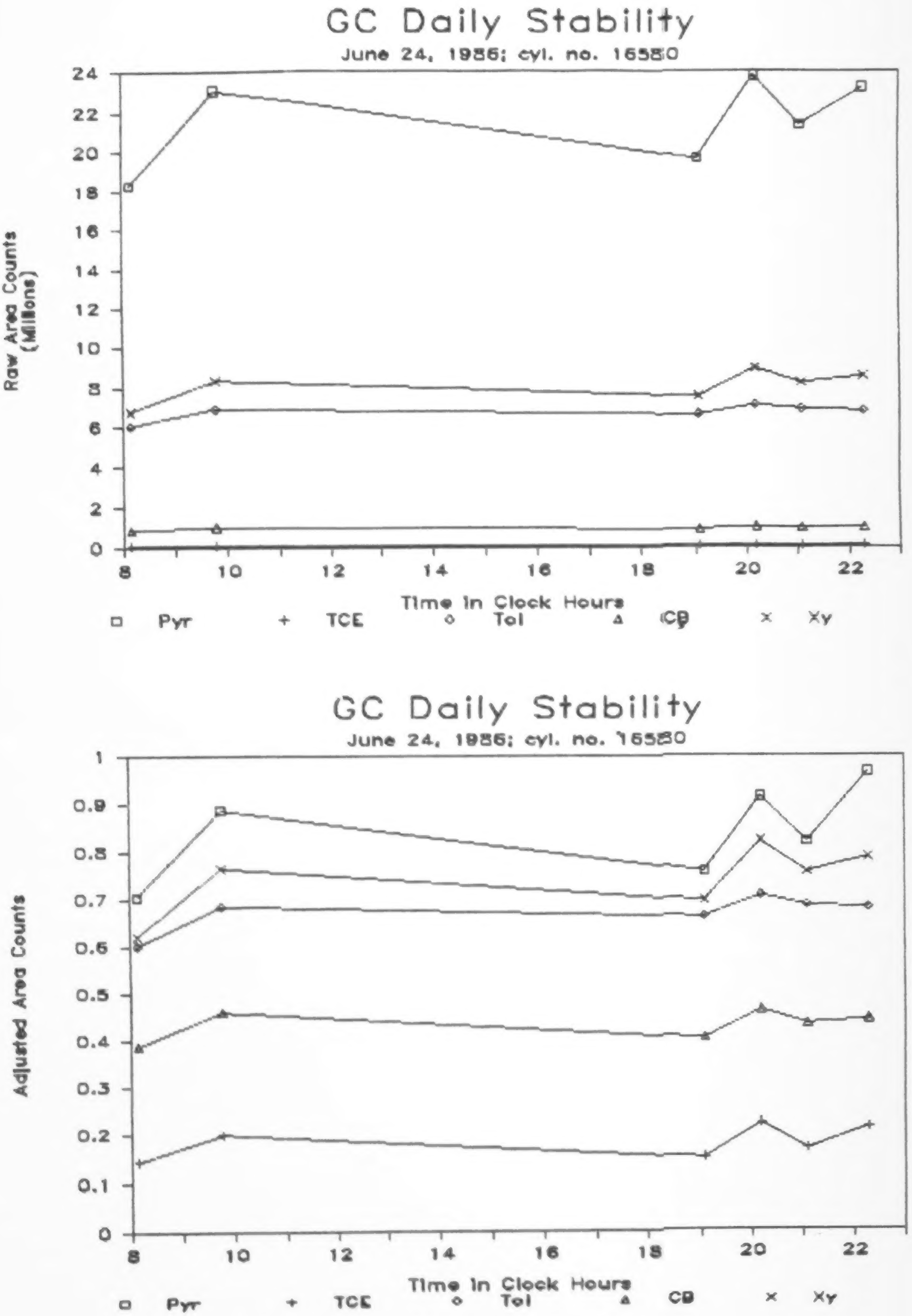


Figure C-13. GC response vs. time.

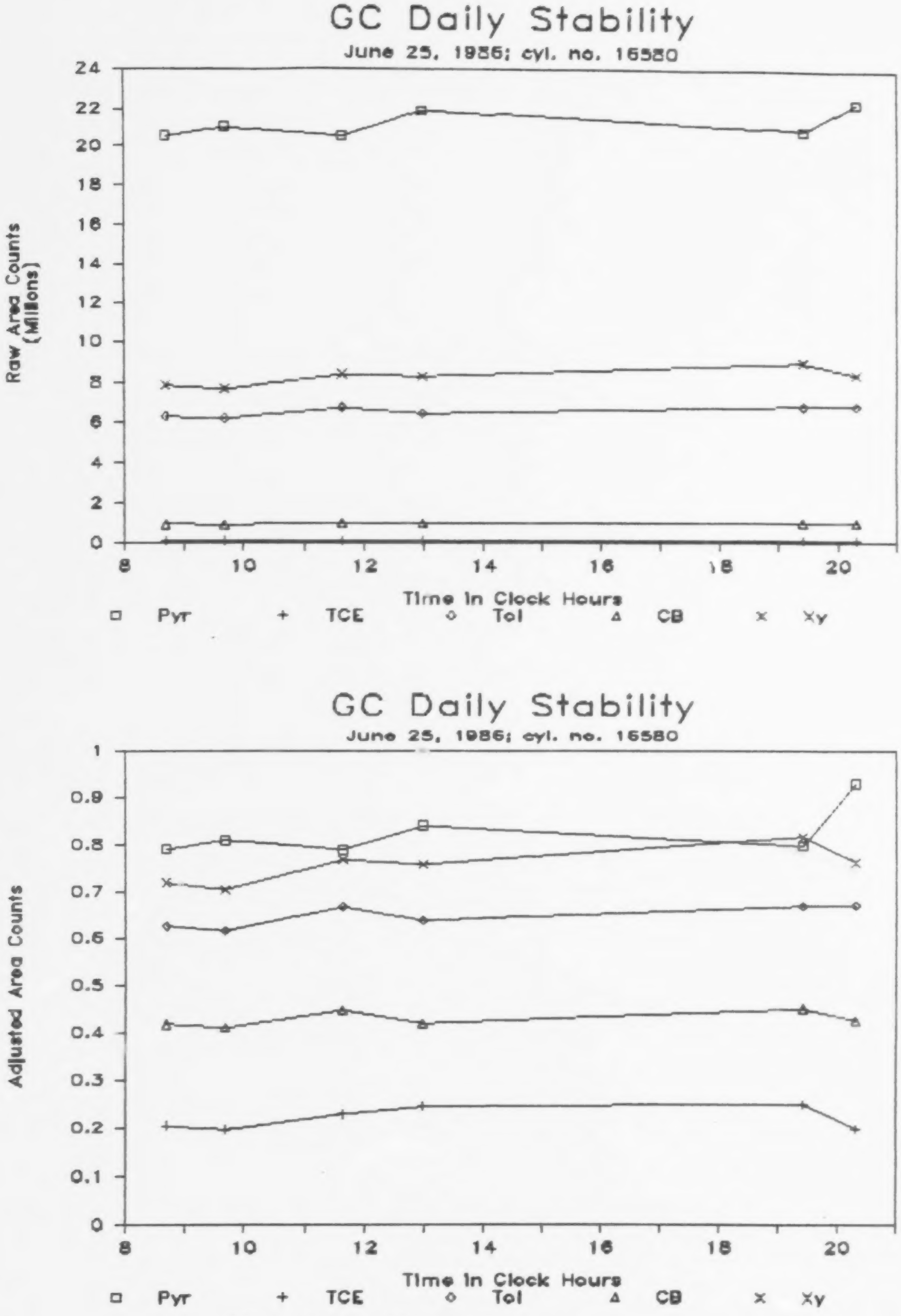
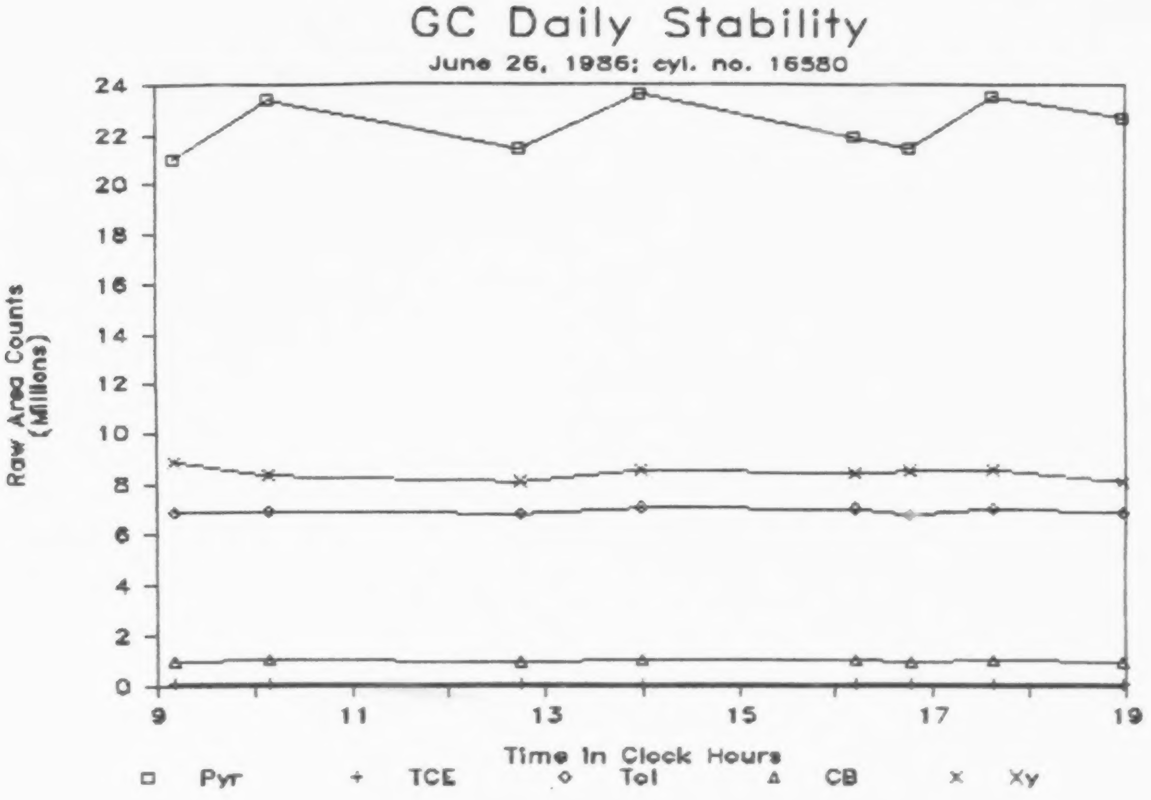


Figure C-14. GC response vs. time.



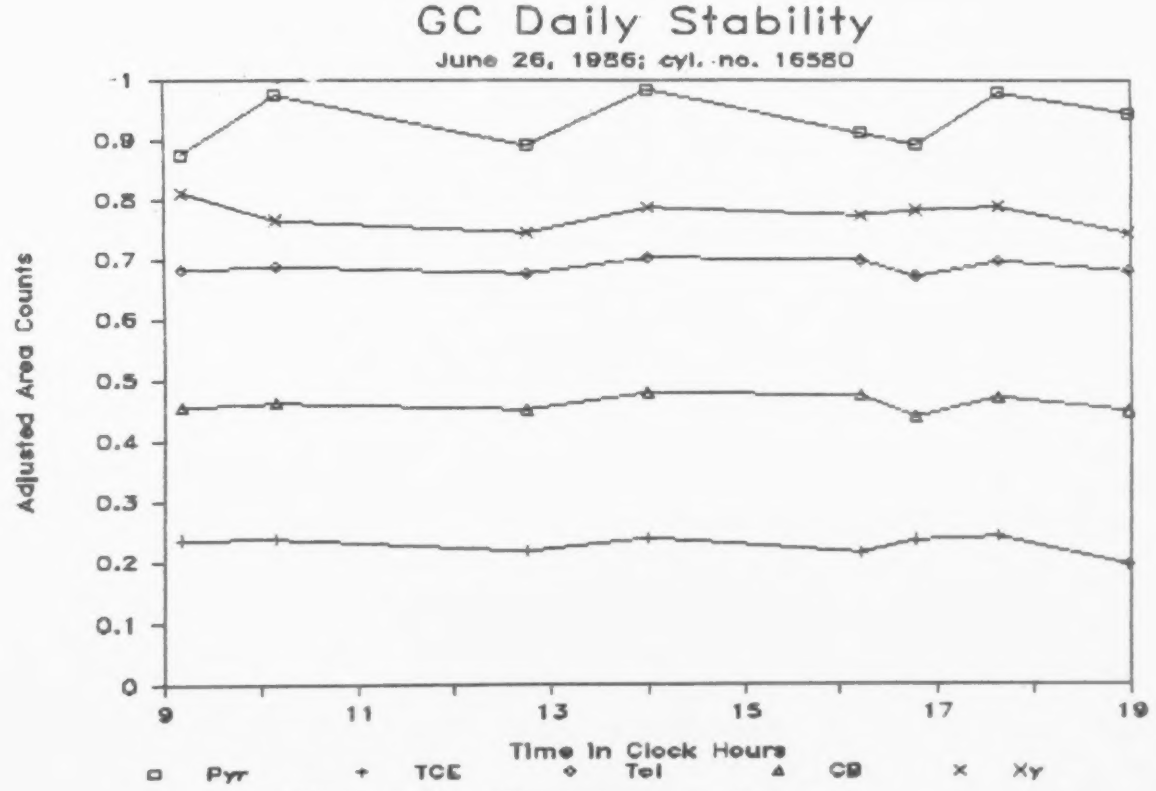


Figure C-15. GC response vs. time.

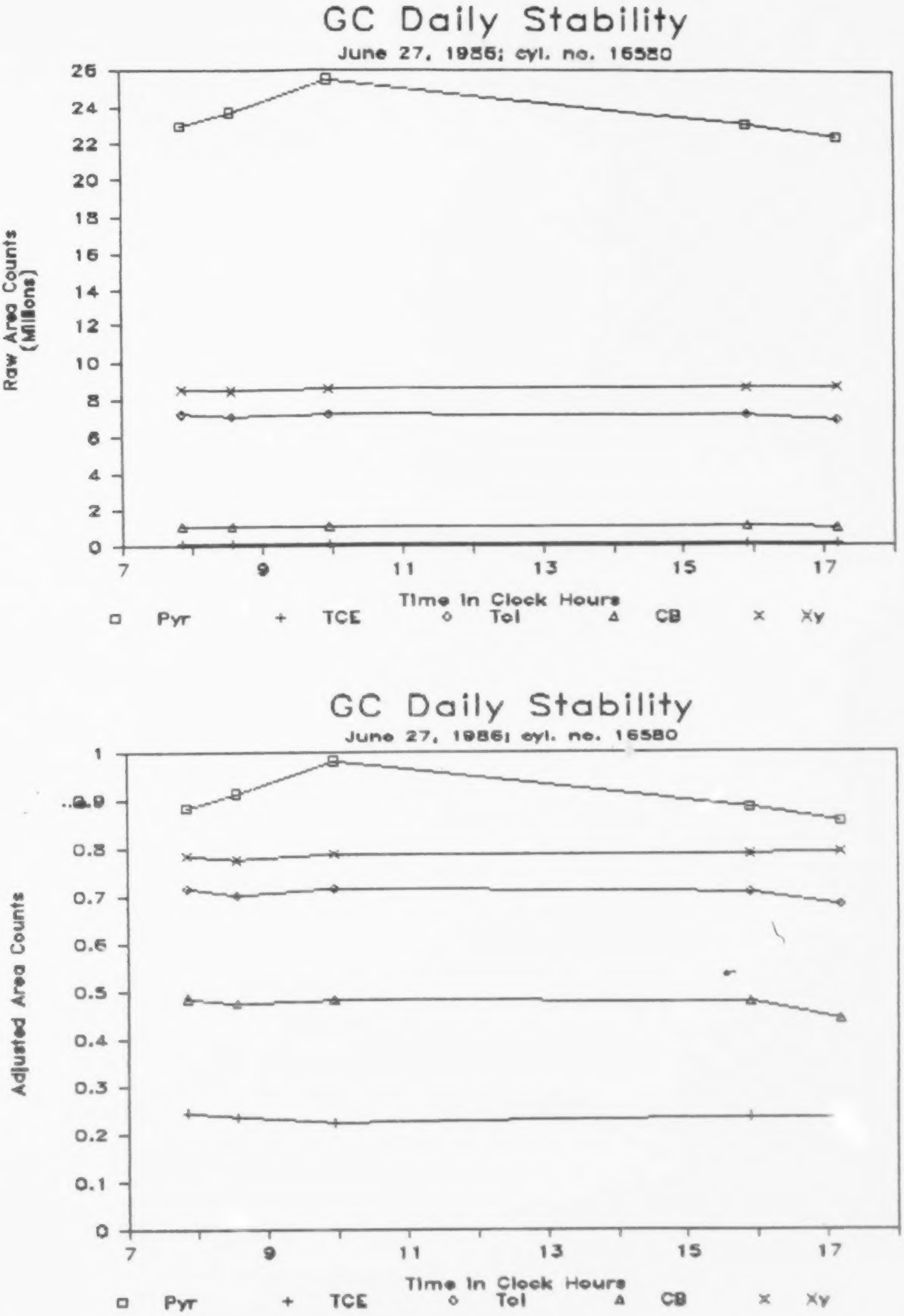


Figure C-16. GC response vs. time.

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 17, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
8.03	1242508		414018	59137	437640
8.55	1280716		409371	58029	433749
13.08	1207833		383002	54388	403525
19.82	1109911		346424	49502	374201
20.27	1206782		369642	52258	425602
23.25	1202501		374052	52604	409696
25.58	1288434	1370	405454	56697	468380
mean	1219812	1370	385995	54659	421828
std	55581		22976	3212	27578
rsd	4.56%		5.95%	5.88%	6.54%
ppm	586.600	5.660	110.500	19.730	99.170
rf	4.809E-04	4.131E-03	2.863E-04	3.610E-04	2.351E-04

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Train A Cylinder #: 16527

Time in Clock Hours	Area Counts Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
17.02	974470	771	327359	39790	321619
17.27	1016998	651	328192	40641	334143
23.72	1060402	1307	348488	41374	379635
mean	1017290	910	334680	40602	345132
std	35082	285	9770	647	24927
rsd	3.45%	31.35%	2.92%	1.59%	7.22%
ppm	489.208	3.758	95.810	14.656	81.139
Scott	548.500	6.758	108.000	16.620	97.690
% of expcted	89.19%	55.61%	88.71%	88.18%	83.06%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 12584 Date: June 17, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 16527

Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
	Area Counts				
15.25	108853		332948	40991	328086
15.50	962161		322173	38998	312171
16.25	783509		318389	38718	315503
18.07	973877	1182	324218	39385	312652
24.38	1139384	1854	374633	45455	396483
mean	964733	1518	334472	40709	332979
std	360405	336	20641	2500	32275
rsd	37.36%	22.13%	6.17%	6.14%	9.69%
ppm	463.934	6.271	95.750	14.695	78.282
Scott	548.500	6.758	108.000	16.620	97.690
% of expected	84.58%	92.80%	88.66%	88.42%	80.13%

* * *

Train C Cylinder #: 16580

Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
	Area Counts				
17.52	1013021	644	321046	41346	325927
17.82	1036186	1139	331758	43821	348306
23.93	1113668	1713	356359	44253	383285
mean	1074927	1165	336388	43140	352506
std	43037	437	14783	1281	23604
rsd	4.00%	37.48%	4.39%	2.97%	6.70%
ppm	516.926	4.814	96.299	15.572	82.873
Scott	547.900	6.313	106.100	17.090	97.400
% of expected	94.35%	76.26%	90.76%	91.12%	85.08%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 17, 1986

Size of gas sample: 1.1 mL

Train D Cylinder #: 16580

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
15.77	1003715		319947	40622	326416
16.50	987062	1126	315179	41763	320604
23.48	1159388	1636	360450	48101	393748
mean	1073225	1381	331859	43495	346923
std	77608	255	20311	3290	33195
rsd	7.23%	18.46%	6.12%	7.56%	9.57%
ppm	516.107	5.705	95.002	15.700	81.560
Scott	547.900	6.313	106.100	17.090	97.400
% of expected	94.20%	90.38%	89.54%	91.87%	83.74%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 19, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.37	24726756	34898	7607226	1077297	7434318
13.15	22594633	26538	6438095	945991	7138150
18.93	24080427	75150	8760498	1357165	11651460
mean	23800605	45529	7601940	1126818	8741309
std	892641	21222	948124	171474	2061336
rsd	3.75%	46.61%	12.47%	15.22%	23.58%
ppm	586.600	5.660	110.500	19.730	99.170
rf	2.465E-05	1.243E-04	1.454E-05	1.751E-05	1.134E-05

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
19.73	44044570	53777	12751618	2004989	17401748
22.42	58693546	81780	14803619	2740335	22119227
25.38	53229785	85509	14344359	2497538	20692459
mean	55961666	83645	14573989	2618937	21405843
std	2731881	1865	229630	121399	713384
rsd	4.88%	2.23%	1.58%	4.64%	3.33%
ppm	586.600	5.660	110.500	19.730	99.170
rf	1.048E-05	6.767E-05	7.582E-06	7.534E-06	4.633E-06

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 19, 1986

Size of gas sample: 1.1 mL

Train A Cylinder #: 16527

Area Counts

Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	c-Xylene
10.80	21821709	48719	6279801	782138	7119454
11.58	22987476	49005	6601210	846785	7366596
mean	22404593	48862	6440506	814462	7243025
std	582884	143	160705	32324	123571
rsd	2.60%	0.29%	2.50%	3.97%	1.71%
ppm	552.193	6.074	93.618	14.261	82.172

Area Counts

Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	c-Xylene
23.85	42526605	204724	13372333	2073847	17589158
ppm	445.771	13.853	101.389	15.624	81.488
avg ppm	498.982	9.964	97.503	14.942	81.830
Scott	548.500	6.758	108.000	16.620	97.690
% of expcted	90.97%	147.44%	90.28%	89.90%	83.76%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 19, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 16527

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
10.33	21360552	43113	6355721	784550	7137384
11.13	22048390	45892	6488432	827860	7320507
mean	21704471	44503	6422077	806205	7228946
std	343919	1390	66356	21655	91562
rsd	1.58%	3.12%	1.03%	2.69%	1.27%
ppm	534.938	5.532	93.350	14.116	82.012

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
23.28	53333814	153624	11704362	1497613	13988279
ppm	559.054	10.395	88.742	11.282	64.806
avg ppm	546.996	7.964	91.046	12.699	73.409
Scott	548.500	6.758	108.000	16.620	97.690
% of expcted	99.73%	117.84%	84.30%	76.41%	75.14%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 19, 1986

Size of gas sample: 1.1 mL

Train C Cylinder #: 16580

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.62	19954829	41239	5739746	703110	6428866
11.37	23014457	46083	6419127	848898	6968037
12.18	21207492	38506	6091895	800633	6482330
mean	21392259	41943	6083589	784214	6626411
std	1255902	3133	277418	60640	242550
rsd	5.87%	7.47%	4.56%	7.73%	3.66%
ppm	527.243	5.214	88.430	13.731	75.177

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
19.43	31300862	322808	10866580	1544329	15092363
21.90	51818169	176489	13943599	2428078	19184123
24.15	53413952	218657	12180921	1564013	14288975
mean	45510994	239318	12330367	1845473	16188487
std	10069178	61495	1260625	412042	2143476
rsd	22.12%	25.70%	10.22%	22.33%	13.24%
ppm	477.054	16.194	93.489	13.903	74.999
avg ppm	502.149	10.704	90.959	13.817	75.088
Scott	547.900	6.313	106.100	17.090	97.400
% of expcted	91.65%	169.56%	85.73%	80.85%	77.09%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 11584 Date: June 19, 1986

Size of gas sample: 1.1 mL

Train D Cylinder #: 16580

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.85	19236908	28829	5751976	706914	5724090
10.58	21960867	43466	6245922	818274	7232679
12.75	17501202	29303	5837849	759340	6849677
mean	19566326	33866	5945249	761509	6602149
std	1835491	6791	215479	45488	640267
rsd	9.38%	20.05%	3.62%	5.97%	9.70%
ppm	482.240	4.210	86.419	13.334	74.901

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
19.17	32647101	169776	11954197	1889124	16208223
22.13	55728940	191579	13779771	2313418	18673206
23.50	43311076	188941	11851551	1674045	14482768
mean	43895706	183432	12528506	1958862	16454732
std	9432185	9716	885770	265640	1719596
rsd	21.49%	5.30%	7.07%	13.56%	10.45%
ppm	460.122	12.412	94.991	14.757	76.232
avg ppm	471.181	8.311	90.705	14.045	75.567
Scott	547.900	6.313	106.100	17.090	97.400
% of expcted	86.00%	131.65%	85.49%	82.19%	77.58%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 20, 1986

Size of gas sample: 1.1 ml

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
13.23	21297419	98139	6321741	932884	8119653
15.60	22405916	103187	6264648	901974	7692618
17.03	20999784	106791	6236510	898015	7640756
19.58	21329635	96070	6130545	866671	7889190
22.78	20321008	72709	6180008	852149	7671566
27.07	21211844	104120	6176862	905660	8191848
mean	21260934	96836	6218386	892892	7867605
std	615238	11379	63330	26516	219712
rsd	2.89%	11.75%	1.02%	2.97%	2.79%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.577E-05	6.519E-05	1.706E-05	1.914E-05	1.238E-05

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Train A Cylinder #: 16527

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
15.35	20051499	80470	6271187	884735	6909526
18.82	18704205	81299	5855673	756046	6886558
21.98	17966822	76927	6200331	866763	6948273
25.98	18242381	68929	5964054	764064	6876763
mean	18741227	76906	6072811	817902	6905280
std	801051	4890	169257	58264	27523
rsd	4.27%	6.36%	2.79%	7.12%	0.40%
ppm	482.966	5.014	103.616	15.655	85.487
Scott	548.500	6.758	108.000	16.620	97.690
% of expcted	88.05%	74.19%	95.94%	94.19%	87.51%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 20, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 16527

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
14.05	7519955	80248	5771387	753253	6064568
14.90	17822575	67867	6228421	854807	7249354
18.13	18848340	75702	5974335	809855	6794920
19.05	19138672	79206	5994178	813221	6846816
22.45	18100075	71004	6046734	817908	6747599
25.50			8493752	1415652	6395845
26.85	20566310	87650	6276113	829216	7255330
mean	18895194	76946	6048528	813043	6764919
std	962999	6453	168040	30590	398173
rsd	5.10%	8.39%	2.78%	3.76%	5.89%
ppm	486.934	5.016	103.202	15.562	83.749
% of expcted	88.78%	74.23%	95.56%	93.63%	85.73%

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Train C Cylinder #: 9188

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
14.30	19269497	88398	5910438	825821	6616276
15.13	20374227	95618	6125674	964435	6823546
17.92	18900984	98635	6009809	922153	6482622
19.28	19349015	88925	5886279	884091	6751263
26.20	19686297	86704	6042729	852155	7158463
mean	19577631	91656	5994986	889731	6766434
std	496477	4626	87800	49316	228156
rsd	2.54%	5.05%	1.46%	5.54%	3.37%
ppm	504.521	5.975	102.288	17.029	83.768
Scott	592.800	8.034	108.600	19.280	100.300
% of					

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 20, 1986

Size of gas sample:	1.1 mL				
expcted	85.11%	74.38%	94.19%	88.33%	83.52%

Train D Cylinder #: 9188

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
14.55	20054754	89052	5912798	868192	6401379
18.40	19078008	95441	5860525	871007	6841886
22.22	19509637	84904	6148730	935392	6645508
25.73	19495733	84916	6191312	928686	6627894
mean	19534533	88578	6028341	900819	6629167
std	346832	4308	143671	31325	156049
rsd	1.78%	4.86%	2.38%	3.48%	2.35%
ppm	503.410	5.775	102.857	17.242	82.068
Scott	592.800	8.034	108.600	19.280	100.300
% of expcted	84.92%	71.88%	94.71%	89.43%	81.82%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 23, 1986

Size of gas sample: 1.1 mL

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.12	24021450	117461	7070879	1056819	8671944
11.93	23994727	125265	7005165	1044196	8127415
12.42	23817487	124285	6887918	1001303	8256040
16.38	22205795	129269	6870242	1017417	8555392
18.83			6833510	967634	8395621
20.10	23738152	110241	7046309	1009001	8218564
mean	23555522	121304	6952337	1016062	8370829
std	683188	6711	91908	29062	191903
rsd	2.90%	5.53%	1.32%	2.86%	2.29%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.326E-05	5.204E-05	1.526E-05	1.682E-05	1.164E-05

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Train A Cylinder #: 16527

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
10.98	21328613	108778	6847570	949592	7856769
19.58	22069542	100506	6903508	933443	7510109
mean	21699078	104642	6875539	941518	7683439
std	370465	4136	27969	8075	173330
rsd	1.71%	3.95%	0.41%	0.86%	2.26%
ppm	504.719	5.446	104.928	15.836	89.402
Scott	548.500	6.758	108.000	16.620	97.690
% of expected	92.02%	80.58%	97.16%	95.28%	91.52%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 23, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 16527

Time in Clock Hours	Area Counts: Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
10.40	21096013	111335	6777891	927189	7778650
19.60	22478571	97039	6940142	979875	7951707
mean	21787292	104187	6859017	953532	7865179
std	691279	7148	81126	26343	86529
rsd	3.17%	6.86%	1.18%	2.76%	1.10%
ppm	506.771	5.422	104.676	16.038	91.516
% of expected	92.39%	80.23%	96.92%	96.50%	93.68%

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Train C Cylinder #: 9188

Time in Clock Hours	Area Counts: Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
19.30	21958370	112536	6846849	1001855	7639557
mean	21958370	112536	6846849	1001855	7639557
std	0	0	0	0	0
rsd	0.00%	0.00%	0.00%	0.00%	0.00%
ppm	510.750	5.857	104.490	16.851	88.891
Scott	547.800	6.668	105.900	16.750	96.200
% of expected	93.24%	87.83%	98.67%	100.60%	92.40%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 24, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
8.15	18299438	77041	6073775	851868	6766590
9.77	23061618	107298	6919376	1010469	8330654
19.08	19641791	81006	6666965	885802	7567405
20.18	23745928	119706	7123811	1014180	8945802
21.08	21305031	90678	6913266	950555	8224162
22.28	23147365	114666	6850604	971587	8558746
mean	21533529	98399	6757966	947410	8065560
std	1996850	16412	333915	60488	712855
rsd	9.27%	16.68%	4.94%	6.38%	8.84%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.544E-05	6.416E-05	1.570E-05	1.804E-05	1.208E-05

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Train A Cylinder #: 4295

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.38	21266708	98624	6480875	901213	7180952
19.90	21999670	100569	6797070	925055	7480010
22.07	21804001	103203	6573502	834683	7222489
mean	21690126	100799	6617149	886984	7294484
std	309875	1876	132724	38242	132278
rsd	1.43%	1.86%	2.01%	4.31%	1.81%
ppm	551.884	6.467	103.889	16.000	88.088
Scott	547.800	6.668	105.900	16.750	96.200
% of expected	100.75%	96.98%	98.10%	95.52%	91.57%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 24, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 4295

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
8.95	20449639	105464	6523426	868503	7025842
21.83	22020248	105102	6687805	902332	7173997
mean	21234944	105283	6605616	885418	7099920
std	785305	181	82190	16915	74078
rsd	3.70%	0.17%	1.24%	1.91%	1.04%
ppm	540.303	6.755	103.708	15.972	85.739
% of expected	98.63%	101.30%	97.93%	95.35%	89.13%

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Train C Cylinder #: 14945

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.17	20786585	83727	6543516	875997	6460473
19.65	21829656	108928	6921141	952449	7374493
21.58	21419682	119976	6745741	886327	7322012
mean	21345308	104210	6736799	904924	7052326
std	429067	15170	154294	33869	419051
rsd	2.01%	14.56%	2.29%	3.74%	5.94%
ppm	543.111	6.686	105.768	16.324	85.164
Scott	547.100	6.901	106.500	16.950	96.550
% of expected	99.27%	96.88%	99.31%	96.30%	88.21%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 25, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
8.68	20563853	110928	6320218	919848	7839004
9.68	21045413	106924	6231372	904733	7678564
11.63	20520425	124259	6753948	986778	8379877
12.97	21863471	133678	6450980	925334	8266595
19.42	20764652	136108	6768284	997456	8907097
20.32	22286429	107888	6794229	944080	8323296
mean	21174041	119964	6553172	946372	8232406
std	670374	12005	228385	34466	397469
rsd	3.17%	10.01%	3.49%	3.64%	4.83%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.588E-05	5.262E-05	1.619E-05	1.806E-05	1.183E-05

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Train A Cylinder #: 4295

Time in Clock Hours	Area Counts Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.43	18405466	80049	5857535	775220	6103115
12.63	19224568	87457	6287602	837219	6358921
19.63	20837438	87635	6239526	791156	6847580
mean	19489157	85047	6128221	801198	6436539
std	1010323	3535	192408	26288	308842
rsd	5.18%	4.16%	3.14%	3.28%	4.80%
ppm	504.302	4.476	99.220	14.468	76.153
Scott	547.800	6.668	105.900	16.750	96.200
% of expected	92.06%	67.12%	93.69%	86.38%	79.16%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 25, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 4295

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
8.92	18220749	89198	5618060	719739	6029438
12.40	19610207	85290	6148751	819125	6294527
20.08	20937420	94669	6269580	834398	6726788
mean	19589459	89719	6012130	791087	6350918
std	1109173	3847	282982	50835	288279
rsd	5.66%	4.29%	4.71%	6.43%	4.54%
ppm	506.897	4.721	97.340	14.286	75.140
% of expected	92.53%	70.81%	91.92%	85.29%	78.11%

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Train C Cylinder #: 14945

	Area Counts				
Time in Clock Hours	Pyridine	Tetrachloroethane	Toluene	Chlorobenzene	o-Xylene
9.17	19379355	82297	6131168	819250	6083853
11.88	19311284	101513	6471123	883009	6591871
19.87	20895575	99363	6433257	864565	6664134
mean	19862071	94391	6345183	855608	6446619
std	731326	8597	152119	26789	258205
rsd	3.68%	9.11%	2.40%	3.13%	4.01%
ppm	513.951	4.967	102.733	15.451	76.272
Scott	547.100	6.901	106.500	16.950	96.550
% of expected	93.94%	71.98%	96.46%	91.16%	79.00%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 26, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.18	21038341	128455	6896055	999449	8844243
10.15	23362491	129345	6949571	1018429	8342934
12.75	21382094	118358	6831309	996216	8106679
13.98	23611722	130154	7097766	1057039	8565125
16.22	21839093	117233	7045147	1043245	8415086
16.78	21357319	128256	6779659	970545	8514980
17.63	23468770	131248	7038755	1038555	8576217
18.97	22657766	106283	6878592	989486	8091810
mean	22339700	123667	6939632	1014121	8432134
std	991610	8273	105446	28168	235885
rsd	4.44%	6.69%	1.52%	2.78%	2.80%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.453E-05	5.105E-05	1.529E-05	1.685E-05	1.155E-05

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Train A Cylinder #: 4295

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.43	21094175	98105	6495632	885744	6965322
13.25	20940238	99867	6653218	959414	7341902
16.57	21464403	94385	6656626	966793	7236535
18.05	21643073	95986	6661798	957594	7303791
mean	21285472	97086	6616819	942386	7211888
std	280925	2078	70034	32883	147269
rsd	1.32%	2.14%	1.06%	3.49%	2.04%
ppm	522.044	4.956	101.165	15.881	83.305
Scott	547.800	6.668	105.900	16.750	96.200
% of expcted	95.30%	74.33%	95.53%	94.81%	86.60%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 26, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 4295

Time in Clock Hours	Area Counts Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.67	21097427	99784	6382798	887001	6738493
9.90	20883370	97721	6304700	857331	6789132
13.48	21526756	103303	6693897	953134	7254929
13.75	21394187	106747	6627656	962722	7255126
18.50	20827757	102008	6593912	918093	7221213
18.75	21108236	103927	6544791	924303	7087568
mean	21139622	102248	6524626	917097	7057744
std	251782	2910	137209	36311	215842
rsd	1.19%	2.85%	2.10%	3.96%	3.06%
ppm	518.467	5.220	99.755	15.455	81.524
% of expcted	94.65%	78.28%	94.20%	92.27%	84.74%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 27, 1986

Size of gas sample: 1.1 mL

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
7.85	22940124	132453	7231784	1068089	8542606
8.57	23732912	127403	7099696	1043657	8464706
9.95	25509189	120988	7242687	1061465	8596461
15.90	22976137	128228	7153743	1055729	8586439
17.18	22264593	126790	6895291	979083	8640533
mean	23484591	127172	7124640	1041605	8566149
std	1113914	3673	126083	32275	59512
rsd	4.74%	2.89%	1.77%	3.10%	0.69%
ppm	547.900	6.313	106.100	17.090	97.400
rf	2.333E-05	4.964E-05	1.489E-05	1.641E-05	1.137E-05

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Train A Cylinder #: 14945

Time in Clock Hours	Area Counts				
	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.73	20689596	113819	6767717	928777	7046567
16.93	22084763	126438	6890099	967253	7359746
mean	21387180	120129	6828908	948015	7203157
std	697584	6310	61191	19238	156590
rsd	3.26%	5.25%	0.90%	2.03%	2.17%
ppm	498.967	5.963	101.696	15.554	81.902
Scott	547.100	6.901	106.500	16.950	96.550
% of expected	91.20%	86.41%	95.49%	91.77%	84.83%

TABLE C-5. Measured Concentration of Spike Gas

QC Cylinder number: 16580 Date: June 27, 1986

Size of gas sample: 1.1 mL

Train B Cylinder #: 14945

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.33	20966440	116752	6710852	929636	7099278
16.47	21866011	130580	6991407	981122	7505504
mean	21416226	123666	6851130	955379	7302391
std	449786	6914	140278	25743	203113
rsd	2.10%	5.59%	2.05%	2.69%	2.78%
ppm	499.645	6.139	102.027	15.675	83.031
% of expected	91.33%	88.96%	95.80%	92.48%	86.00%

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Train C Cylinder #: 4295

	Area Counts				
Time in Clock Hours	Pyridine	Tetra-chloro-ethane	Toluene	Chloro-benzene	o-Xylene
9.10	19368394	104375	6588460	908772	7141962
16.70	22022017	113149	6758899	952560	7384903
mean	20695206	108762	6673680	930666	7263433
std	1326812	4387	85220	21894	121471
rsd	6.41%	4.03%	1.28%	2.35%	1.67%
ppm	482.823	5.399	99.384	15.270	82.588
Scott	547.800	6.668	105.900	16.750	96.200
% of expected	88.14%	80.97%	93.85%	91.16%	85.85%

TABLE C-6. Calculation of the Amount of Material Spiked on the XAD-2® Resin

Run No.	Date	Train	Flow Rate	Compound	Concentration	mg on XAD-2®	Standard Deviation
1	86/06/17	A	19.40	d_5-pyridine	489.2	3.914	0.1524
				d_2-tetrachloroethane	3.758	0.0608	0.0191
				d_8-toluene	95.81	0.9123	0.0313
				d_5-chlorobenzene	14.66	0.1647	0.0040
				d_{10}-o-xylene	81.14	0.8961	0.0667
1	86/06/17	B	19.66	d_5-pyridine	463.9	3.761	1.4056
				d_2-tetrachloroethane	6.271	0.1029	0.0228
				d_8-toluene	95.75	0.9239	0.0576
				d_5-chlorobenzene	14.70	0.1673	0.0104
				d_{10}-o-xylene	78.28	0.8761	0.0852
1	86/06/17	C	19.35	d_5-pyridine	516.9	4.125	0.1673
				d_2-tetrachloroethane	4.814	0.0777	0.0291
				d_8-toluene	96.30	0.9145	0.0409
				d_5-chlorobenzene	15.57	0.1745	0.0054
				d_{10}-o-xylene	82.87	0.9129	0.0617
1	86/06/17	D	19.47	d_5-pyridine	516.1	4.1438	0.3005
				d_2-tetrachloroethane	5.705	0.0927	0.0171
				d_8-toluene	95.00	0.9078	0.0558
				d_5-chlorobenzene	15.70	0.1770	0.0134
				d_{10}-o-xylene	81.56	0.9040	0.0667
3	86/06/19	A	19.10	d_5-pyridine	499.0	3.930	0.1421
				d_2-tetrachloroethane	9.964	0.1588	0.0061
				d_8-toluene	97.50	0.9140	0.0324
				d_5-chlorobenzene	14.94	0.1653	0.0078
				d_{10}-o-xylene	81.83	0.8897	0.0270

TABLE C-6. Calculation of the Amount of Material Spiked on the XAD-2® Resin

Run No.	Date	Train	Flow Rate	Compound	Concentration	mg on XAD-2®	Standard Deviation
3	86/06/19	B	19.84	d_5-pyridine	547.0	4.475	0.1014
				d_2-tetrachloroethane	7.964	0.1319	0.0046
				d_8-toluene	91.05	0.8866	0.0170
				d_5-chlorobenzene	12.70	0.1459	0.0046
				d_{10}-o-xylene	73.41	0.8291	0.0171
3	86/06/19	C	19.62	d_5-pyridine	502.1	4.0627	0.2426
				d_2-tetrachloroethane	10.70	0.1753	0.0132
				d_8-toluene	90.60	0.8724	0.0409
				d_5-chlorobenzene	13.82	0.1570	0.0123
				d_{10}-o-xylene	75.00	0.8377	0.0320
3	86/06/19	D	19.40	d_5-pyridine	471.2	3.7694	0.3636
				d_2-tetrachloroethane	8.311	0.1345	0.0271
				d_8-toluene	90.71	0.8636	0.0368
				d_5-chlorobenzene	14.05	0.1578	0.0101
				d_{10}-o-xylene	75.57	0.8345	0.0831
4 & 5	86/06/20	A	19.84	d_5-pyridine	483.0	3.951	0.1748
				d_2-tetrachloroethane	5.014	0.0830	0.0054
				d_8-toluene	103.62	1.009	0.0305
				d_5-chlorobenzene	15.66	0.1799	0.0130
				d_{10}-o-xylene	85.49	0.9655	0.0402
4 & 5	86/06/20	B	20.01	d_5-pyridine	486.9	4.018	0.2081
				d_2-tetrachloroethane	5.016	0.0838	0.0071
				d_8-toluene	103.20	1.013	0.0296
				d_5-chlorobenzene	15.56	0.1803	0.0070
				d_{10}-o-xylene	83.75	0.9540	0.0569

TABLE C-6. Calculation of the Amount of Material Spiked on the XAD-2® Resin

Run No.	Date	Train	Flow Rate	Compound	Concentration	mg on XAD-2®	Standard Deviation
7	86/06/ 24-25	A	20.04 (Day 1) 19.53 (Day 2)	d_5-pyridine	551.9 504.3	25.87	0.6840
				d_2-tetrachloroethane	6.467 4.476	0.5433	0.0116
				d_8-toluene	103.9 99.22	5.919	0.1159
				d_5-chlorobenzene	16.00 14.47	1.048	0.0297
				d_{10}-o-xylene	88.09 76.15	5.555	0.1390
7	86/06/ 24-25	B	20.34 (Day 1) 19.39 (Day 2)	d_5-pyridine	540.3 506.9	25.75	0.9083
				d_2-tetrachloroethane	6.755 4.721	0.5731	0.0126
				d_8-toluene	103.7 97.34	5.885	0.1541
				d_5-chlorobenzene	15.97 14.29	1.0464	0.0353
				d_{10}-o-xylene	85.74 75.14	5.466	0.1358
7	86/06/ 24-25	C	20.10 (Day 1) 19.55 (Day 2)	d_5-pyridine	543.1 514.0	25.94	0.5590
				d_2-tetrachloroethane	6.686 4.97	0.5783	0.0539
				d_8-toluene	105.8 102.7	6.075	0.1086
				d_5-chlorobenzene	16.32 15.45	1.093	0.0279
				d_{10}-o-xylene	85.16 76.26	5.459	0.2047

TABLE C-6. Calculation of the Amount of Material Spiked on the XAD-2® Resin

Run No.	Date	Train	Flow Rate	Compound	Concentration	mg on XAD-2®	Standard Deviation
8 & 9	86/06/26	A	19.83	d_5-pyridine	522.0	4.269	0.0696
				d_2-tetrachloroethane	4.956	0.0820	0.0019
				d_8-toluene	101.2	0.9846	0.0141
				d_5-chlorobenzene	15.88	0.1824	0.0066
				d_{10}-o-xylene	83.31	0.9404	0.0212
8 & 9	86/06/26	B	19.68	d_5-pyridine	518.5	4.2076	0.0656
				d_2-tetrachloroethane	5.220	0.0857	0.0026
				d_8-toluene	99.76	0.9635	0.0222
				d_5-chlorobenzene	15.46	0.1762	0.0072
				d_{10}-o-xylene	81.52	0.9133	0.0293
10	86/06/27	A	20.74	d_5-pyridine	499.0	12.80	0.4185
				d_2-tetrachloroethane	5.963	0.3096	0.0163
				d_8-toluene	101.7	3.1055	0.0289
				d_5-chlorobenzene	15.55	0.5605	0.0115
				d_{10}-o-xylene	81.90	2.901	0.0633
10	86/06/27	B	20.32	d_5-pyridine	499.6	12.56	0.3364
				d_2-tetrachloroethane	6.139	0.3123	0.0182
				d_8-toluene	102.0	3.053	0.0811
				d_5-chlorobenzene	15.68	0.5534	0.0176
				d_{10}-o-xylene	83.03	2.8813	0.0937
10	86/06/27	C	20.65	d_5-pyridine	482.8	12.33	0.7938
				d_2-tetrachloroethane	5.399	0.2791	0.0122
				d_8-toluene	99.38	3.022	0.0640
				d_5-chlorobenzene	15.27	0.5479	0.0159
				d_{10}-o-xylene	82.59	2.913	0.0691

TABLE C-6. Calculation of the Amount of Material Spiked on the XAD-2® Resin

Run No.	Date	Train	Flow Rate	Compound	Concentration	mg on XAD-2®	Standard Deviation
4 & 5	86/06/20	C	20.06	d_5-pyridine	504.5	4.174	0.1223
				d_2-tetrachloroethane	5.975	0.1000	0.0085
				d_8-toluene	102.3	1.007	0.0316
				d_5-chlorobenzene	17.03	0.1978	0.0080
				d_{10}-o-xylene	83.77	0.9566	0.0581
4 & 5	86/06/20	D	19.66	d_5-pyridine	503.4	4.081	0.0750
				d_2-tetrachloroethane	5.775	0.0947	0.0046
				d_8-toluene	102.9	0.9925	0.0240
				d_5-chlorobenzene	17.24	0.1963	0.0069
				d_{10}-o-xylene	82.07	0.9185	0.0220
6	86/06/23	A	20.61	d_5-pyridine	504.7	6.4344	0.1187
				d_2-tetrachloroethane	5.446	0.1405	0.0031
				d_8-toluene	104.93	1.592	0.0370
				d_5-chlorobenzene	15.84	0.2835	0.0127
				d_{10}-o-xylene	89.40	1.5734	0.0339
6	86/06/23	B	21.16	d_5-pyridine	506.8	6.633	0.4823
				d_2-tetrachloroethane	5.422	0.1436	0.0090
				d_8-toluene	104.7	1.631	0.1040
				d_5-chlorobenzene	16.04	0.2948	0.0193
				d_{10}-o-xylene	91.52	1.6535	0.1049
6	86/06/23	C	20.67	d_5-pyridine	510.8	6.530	0.1533
				d_2-tetrachloroethane	5.857	0.1515	0.0221
				d_8-toluene	104.5	1.590	0.0412
				d_5-chlorobenzene	16.85	0.3026	0.0119
				d_{10}-o-xylene	88.89	1.569	0.0951

The unweighted arithmetic average flow rate and concentrations determined above were used to calculate the quantity of each compound spiked onto the XAD-2®. The calculations assume a temperature of 25°C and an atmospheric pressure of 750 mm Hg. The standard deviation in the amount of material spiked on the XAD was obtained using this equation:

$$(S_R/R)^2 = (S_A/A)^2 + (S_B/B)^2$$

where: S_R = the standard deviation of the quantity spiked on the XAD,

R = the quantity spiked on the XAD,

S_A = the standard deviation of the unweighted arithmetic average of the flow rate,

A = the unweighted arithmetic average of the flow rate,

S_B = the standard deviation of the measured spike concentration,

and

B = the measured spike concentration.

The quantity (S_B/B) was approximated by the unweighted relative standard deviation of the area counts of the spike gas samples. The length of the test was assumed to be exact.

The standard deviation in the amount of material spiked on the XAD for Run 7 was obtained using this equation:

$$(S_{R7})^2 = (S_{R7\ \text{Day}\ 1})^2 + (S_{R7\ \text{Day}\ 2})^2$$

where the subscript 7 indicates Run 7.

The plots showing the stability of the spike component concentrations are shown in Figures C-17 to C-92. Data for each component of the spike gas on each day is on a separate page. The x-axis is in clock-time. The y-axis is in concentration (ppm) and in most cases the scale is expanded. The double lines on the lower portions of the plots indicate the approximate period of time over which sampling was done.

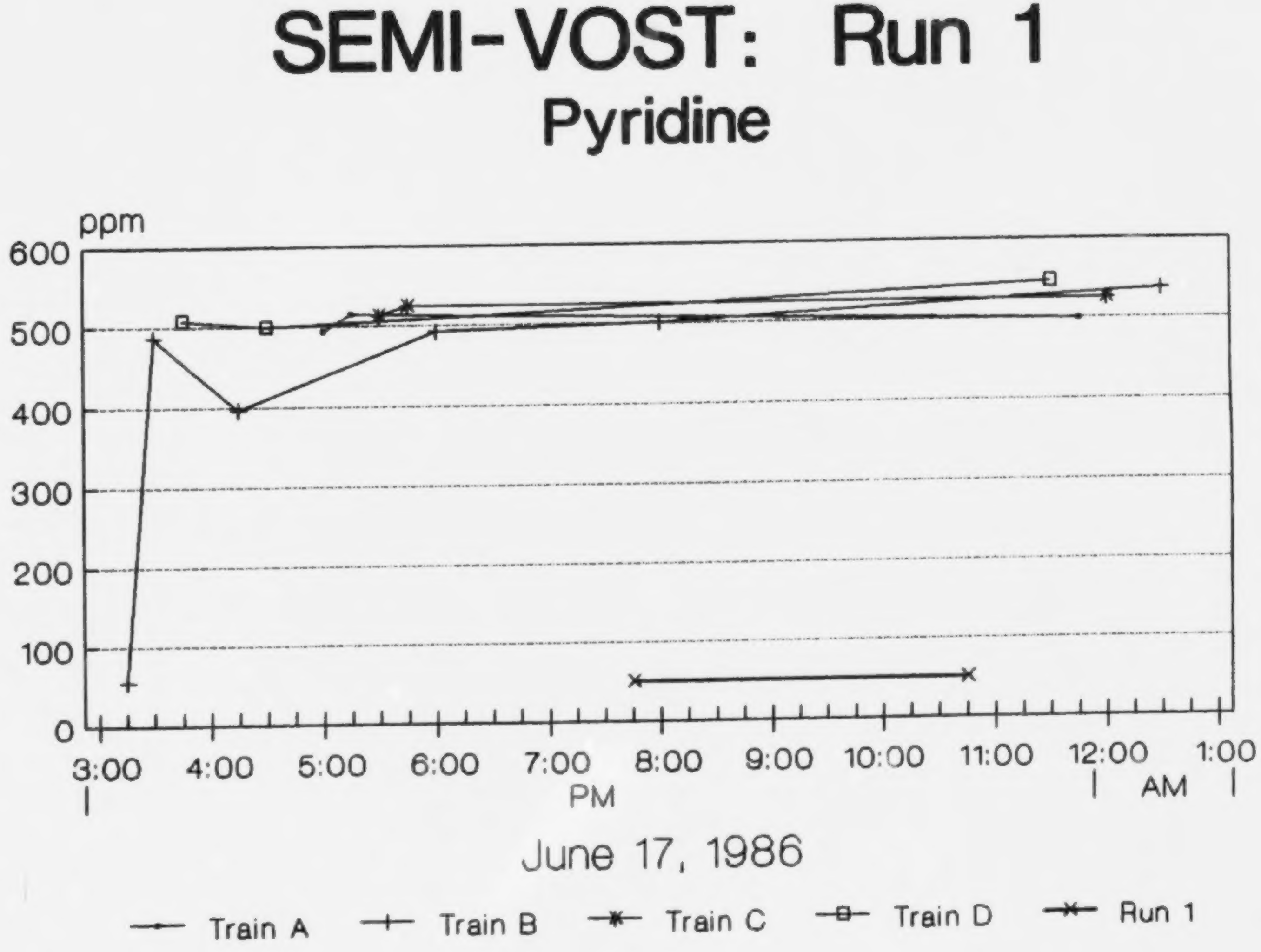


Figure C-17. Concentration vs time.

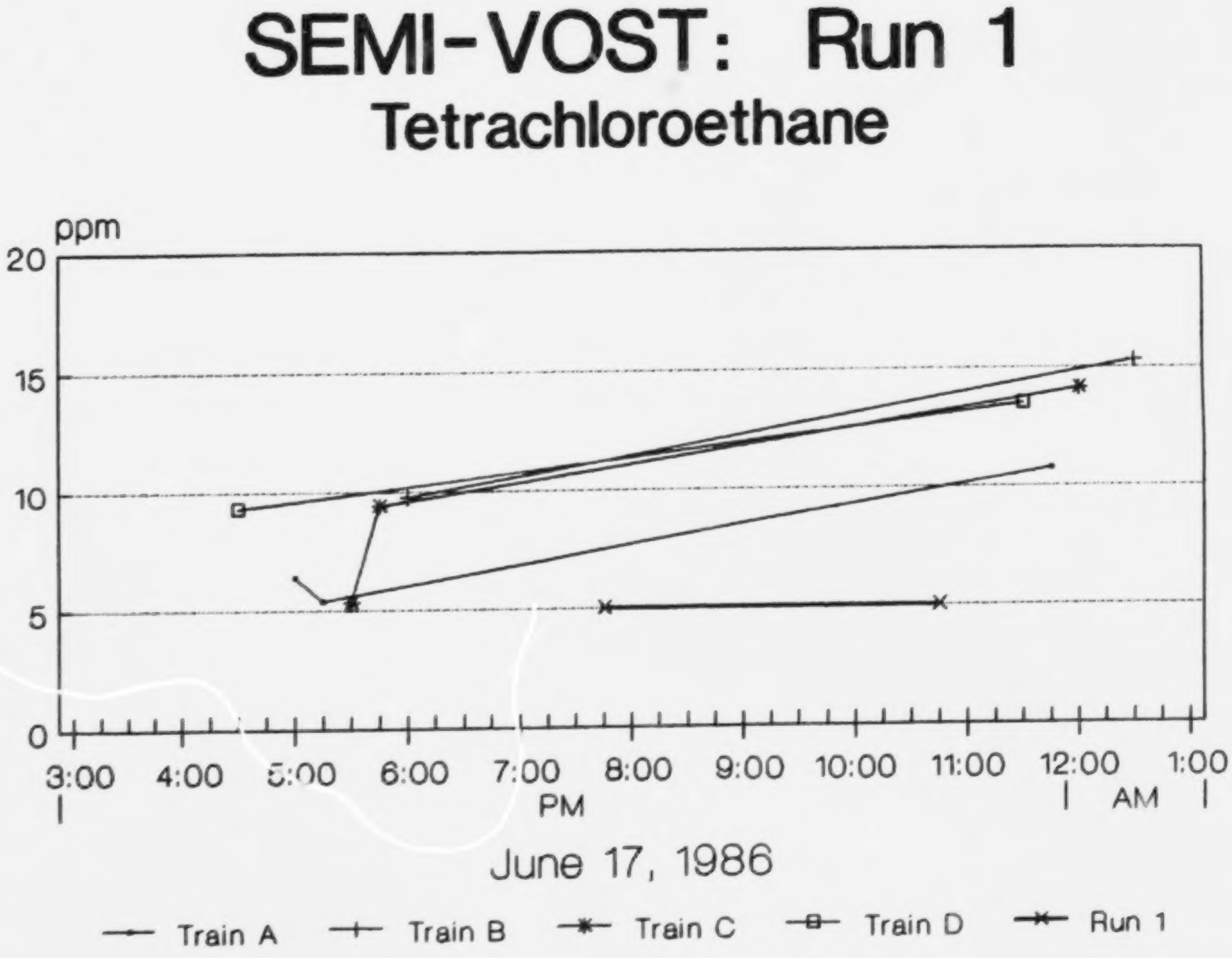


Figure C-18. Concentration vs time.

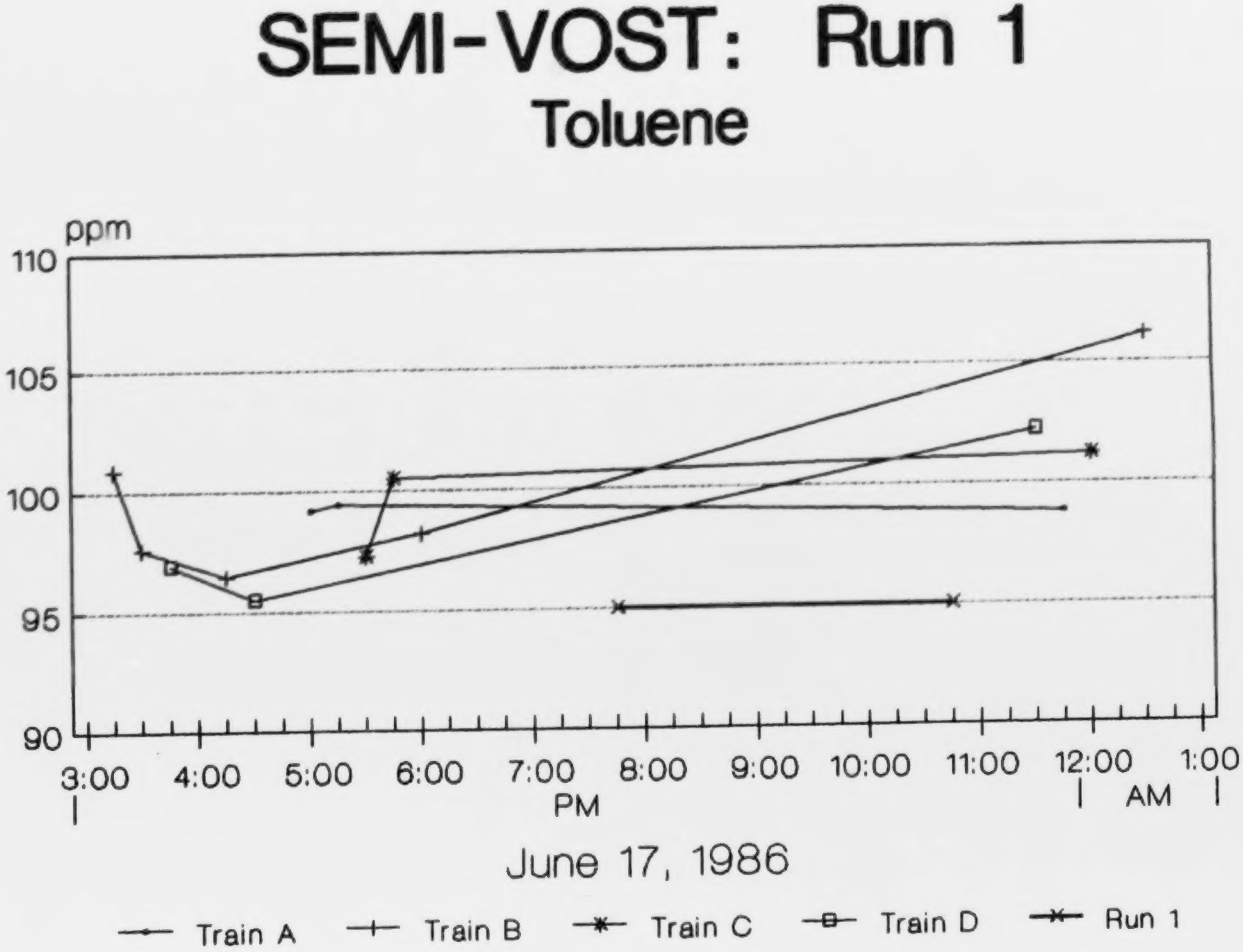
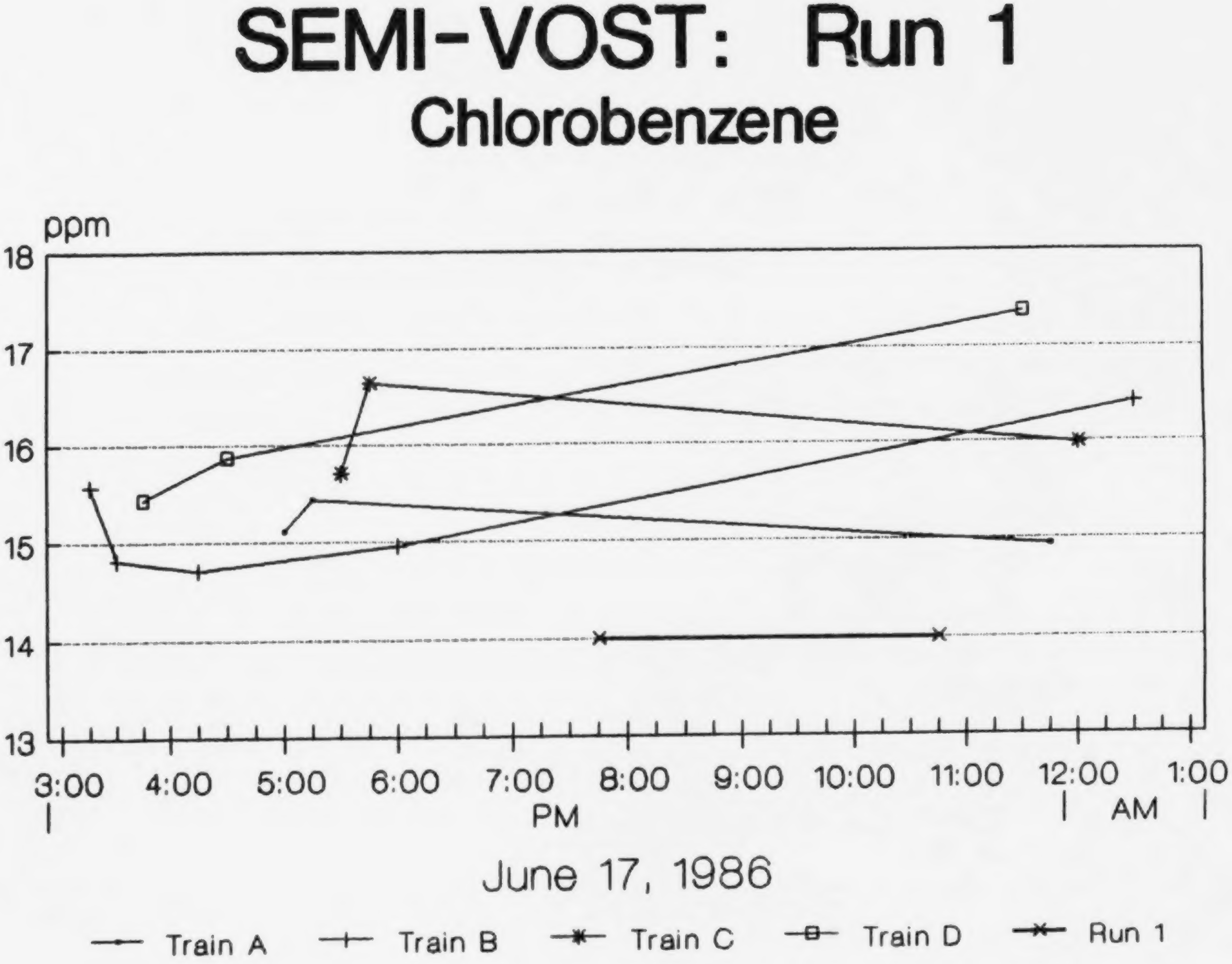


Figure C-19. Concentration vs time.



SEMI-VOST: Run 1
Chlorobenzene

Figure C-20. Concentration vs time.

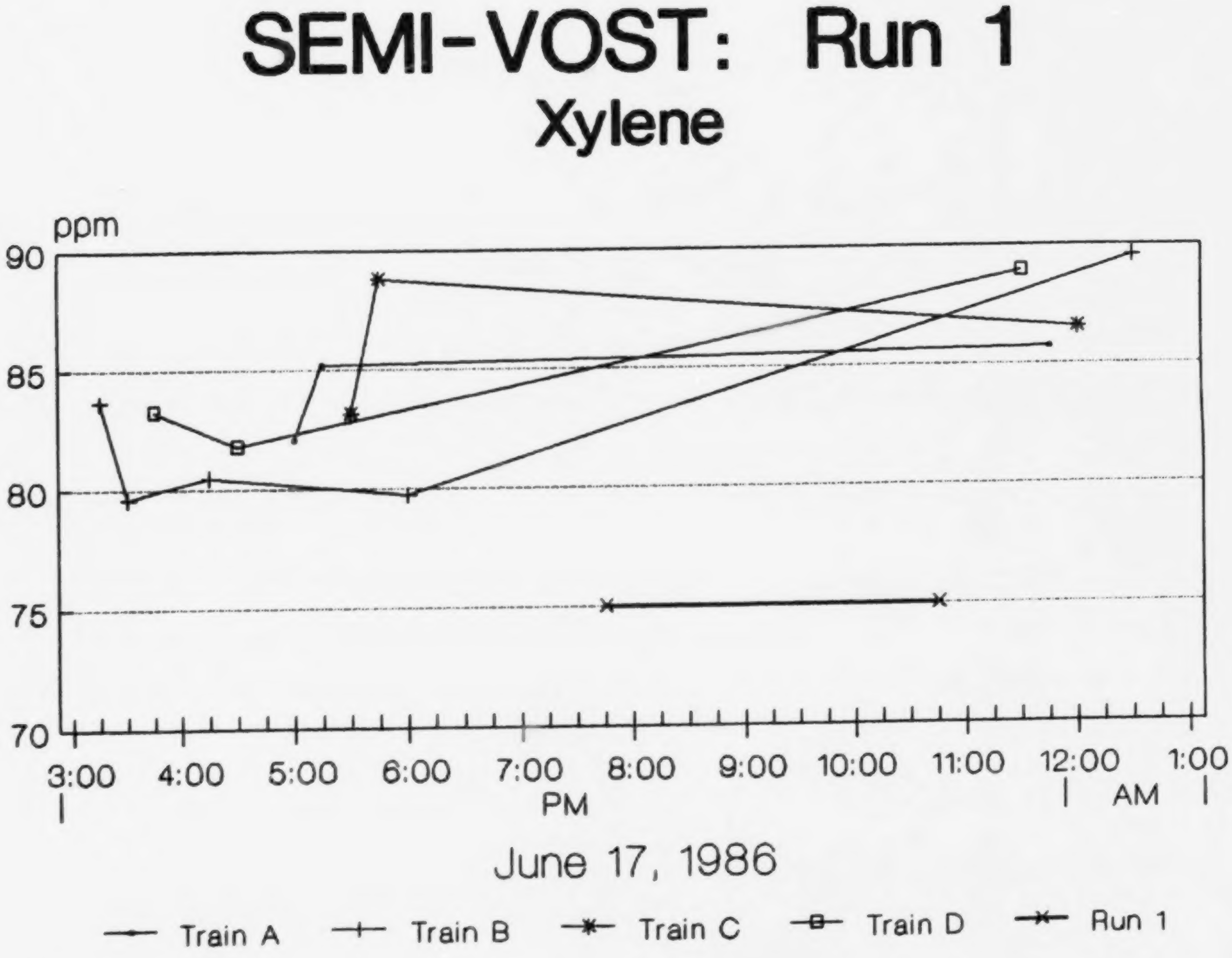


Figure C-21. Concentration vs time.

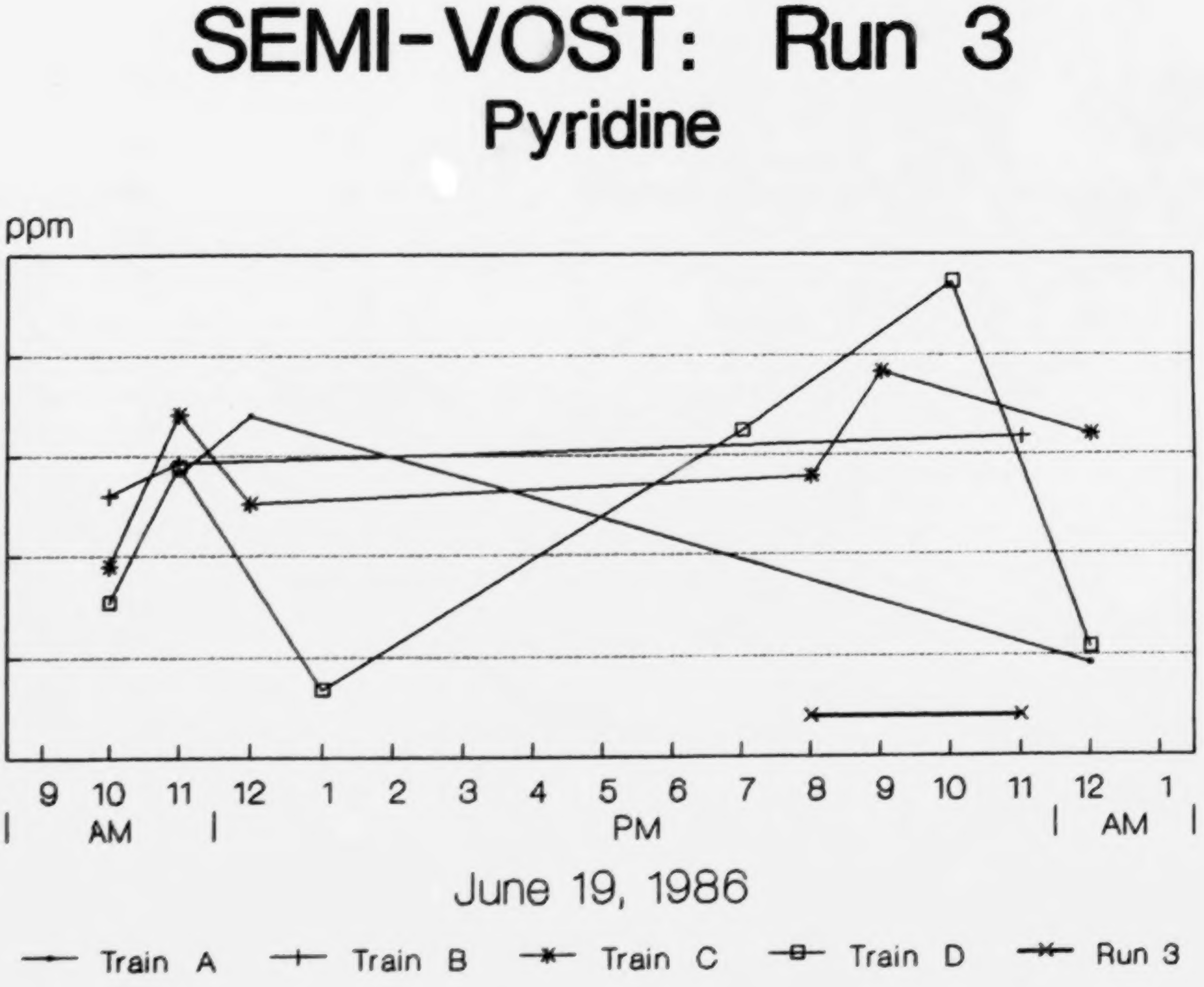
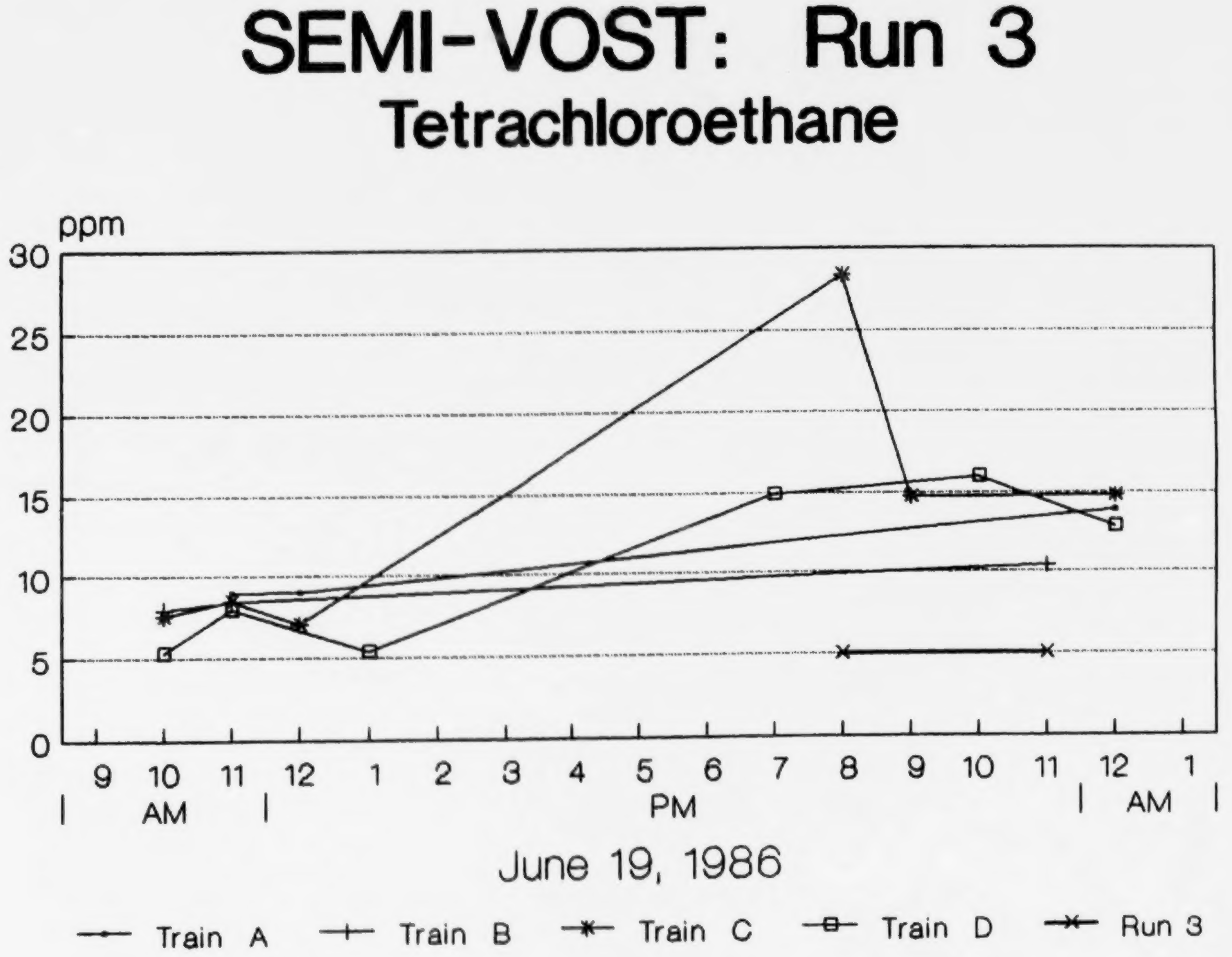


Figure C-22. Concentration vs time.



SEMI-VOST: Run 3
Tetrachloroethane

Figure C-23. Concentration vs time.

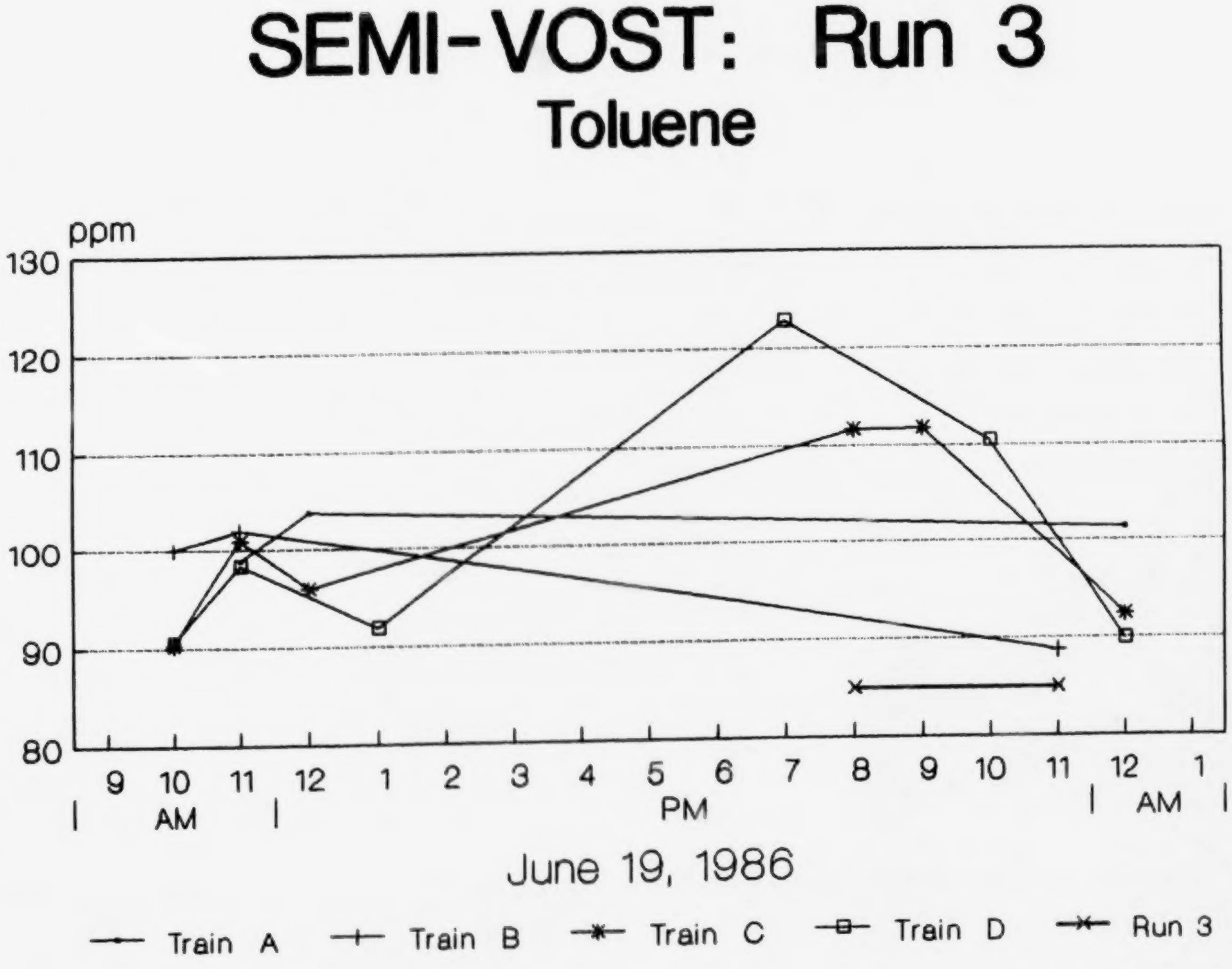

SEMI-VOST: Run 3
Toluene

Figure C-24. Concentration vs time.

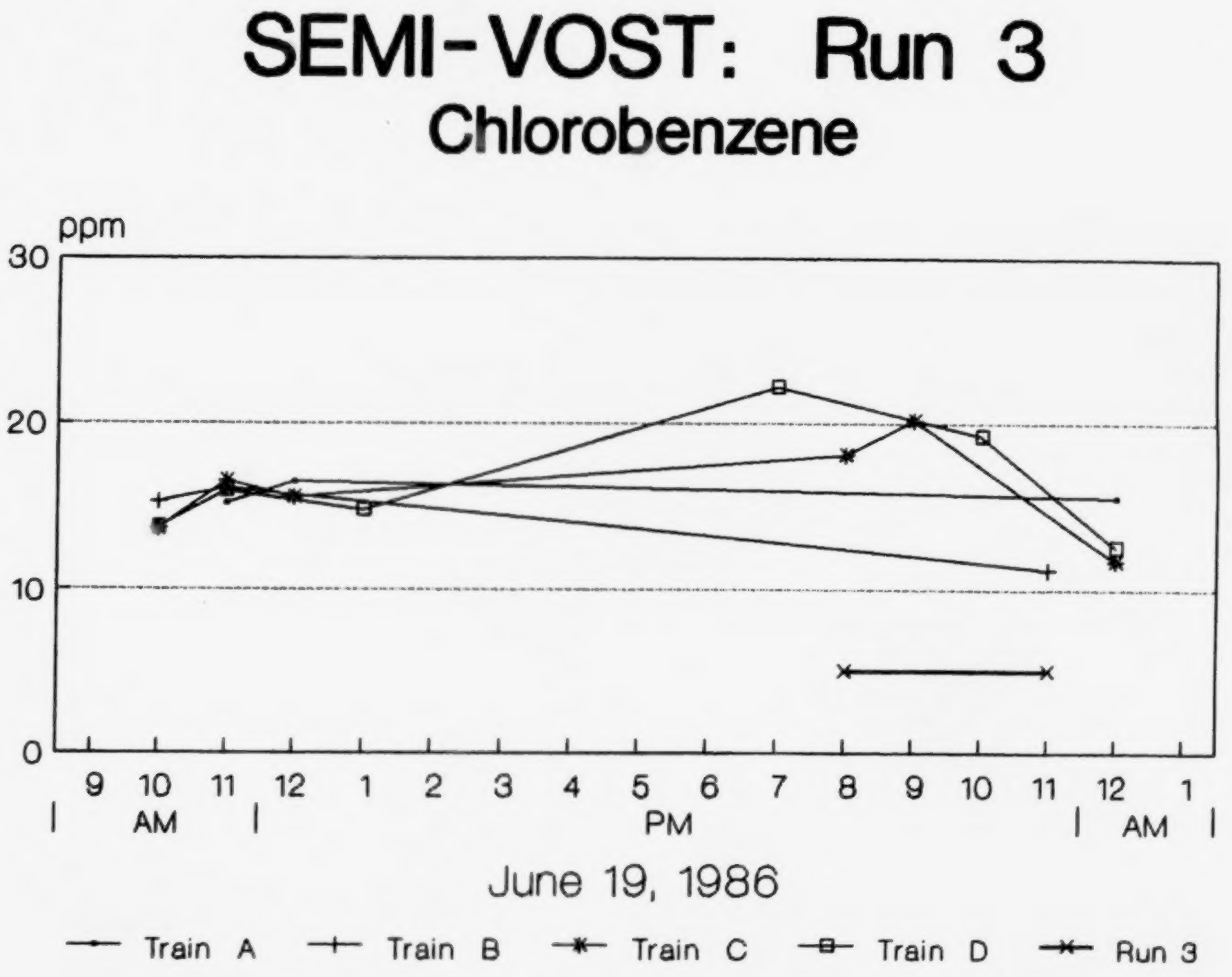
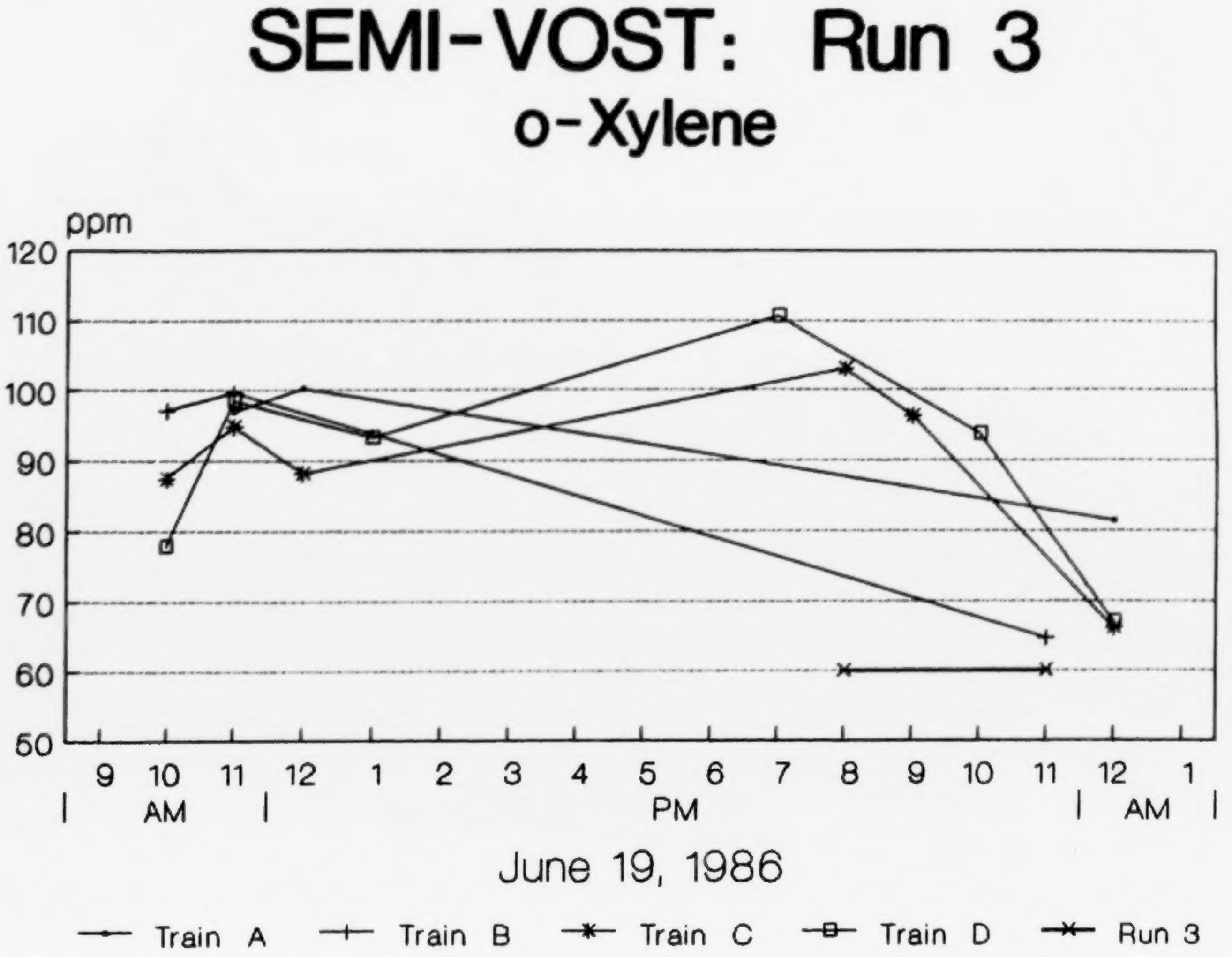


Figure C-25. Concentration vs time.



SEMI-VOST: Run 3

o-Xylene

Figure C-26. Concentration vs time.

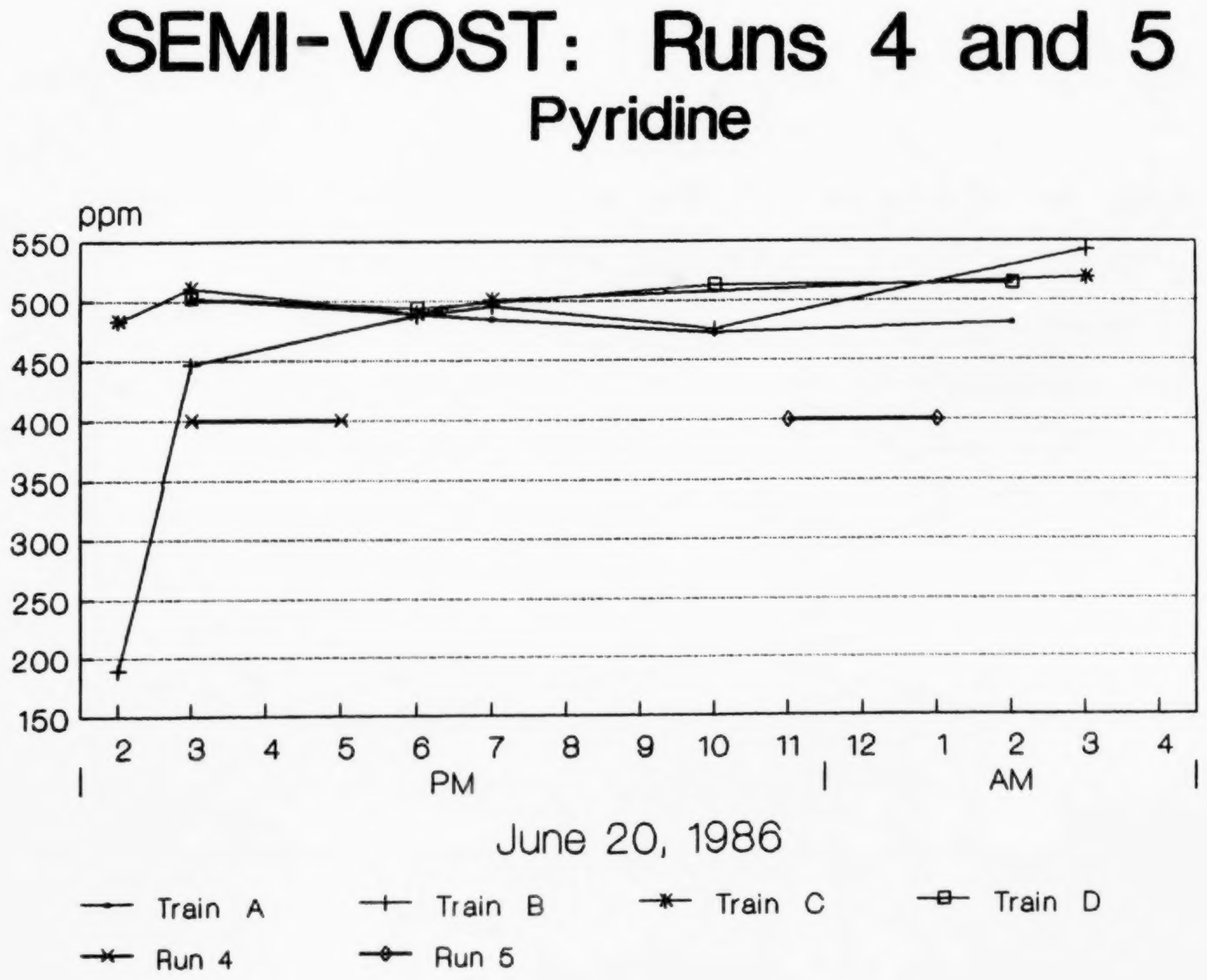


Figure C-27. Concentration vs time.

SEMI-VOST: Runs 4 and 5

Tetrachloroethane

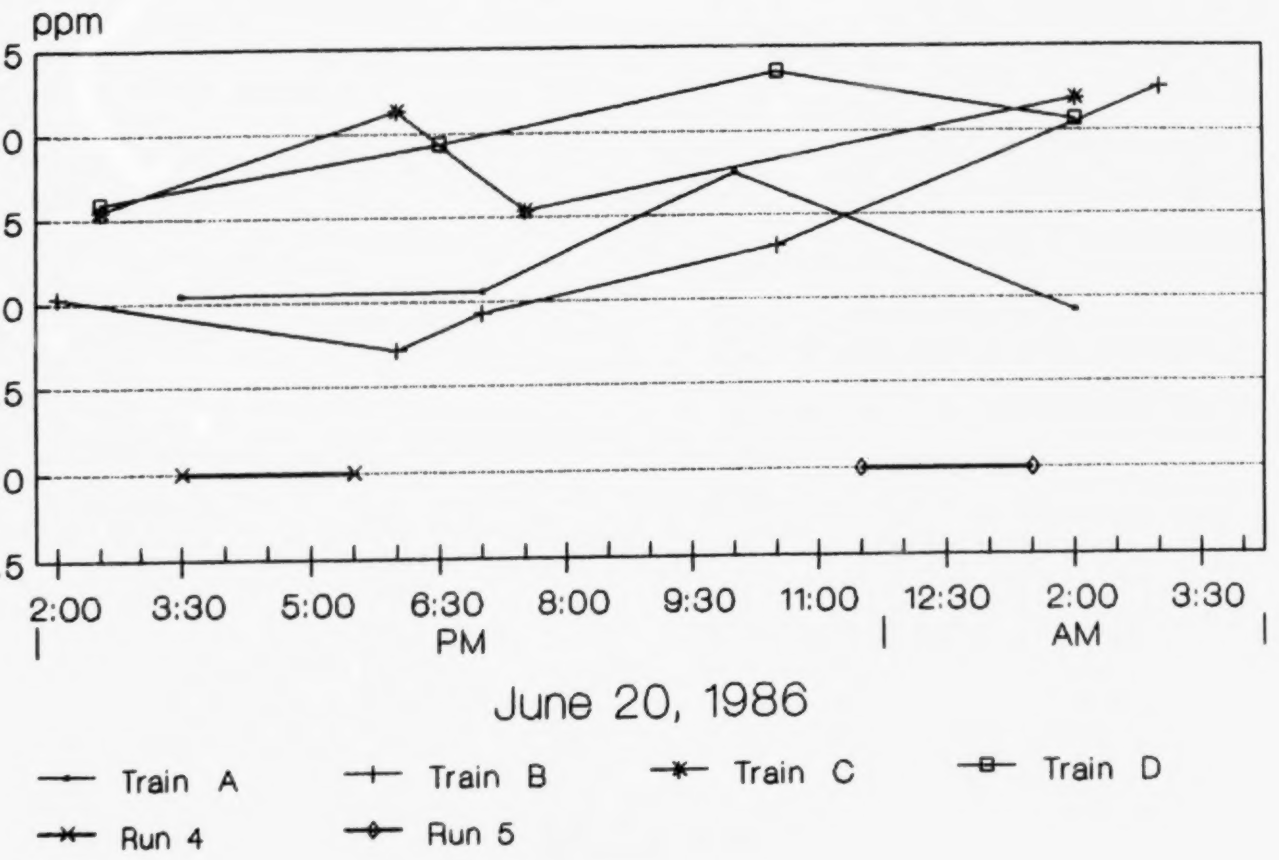


Figure C-28. Concentration vs time.

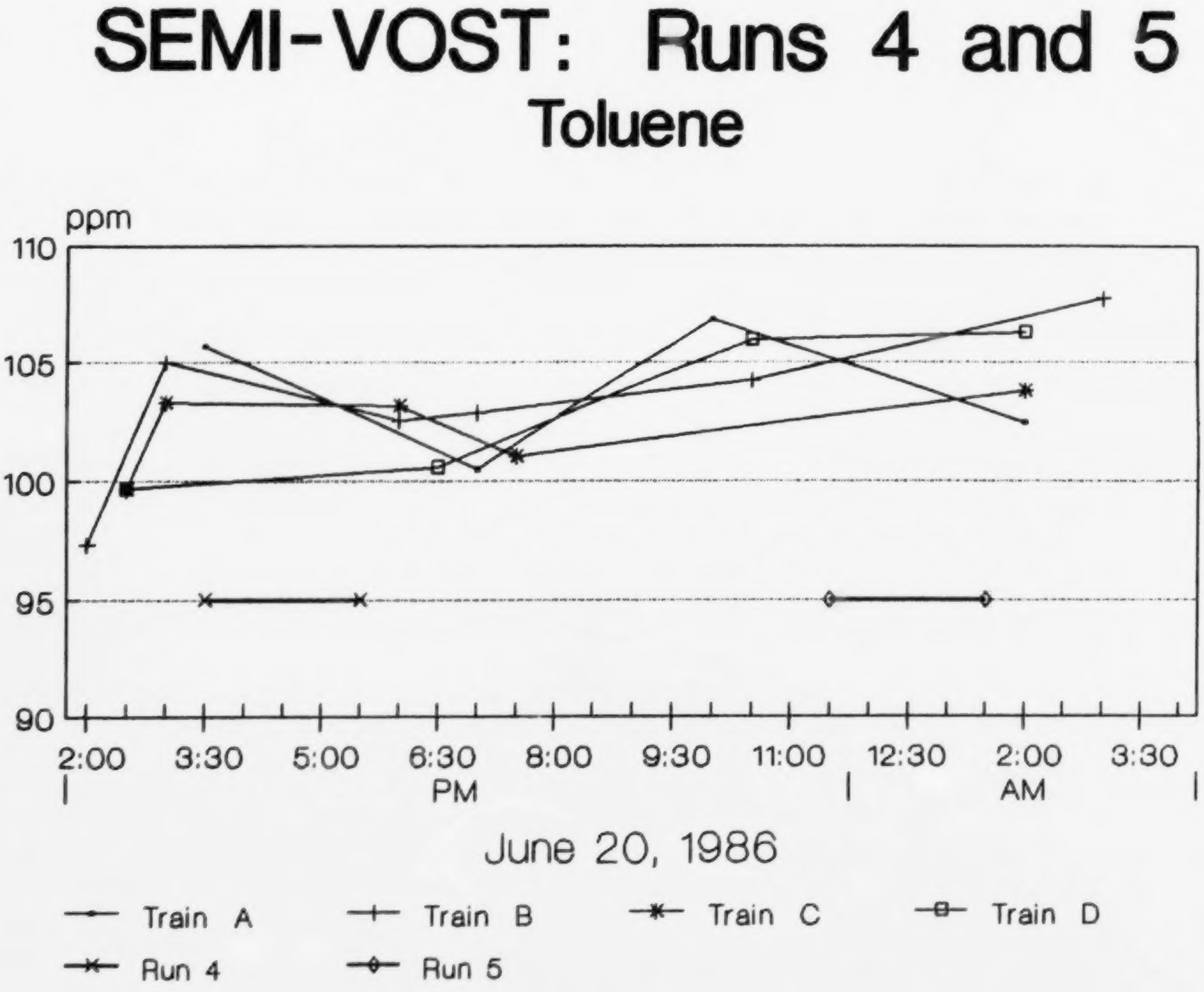


Figure C-29. Concentration vs time.

SEMI-VOST: Runs 4 and 5

Chlorobenzene

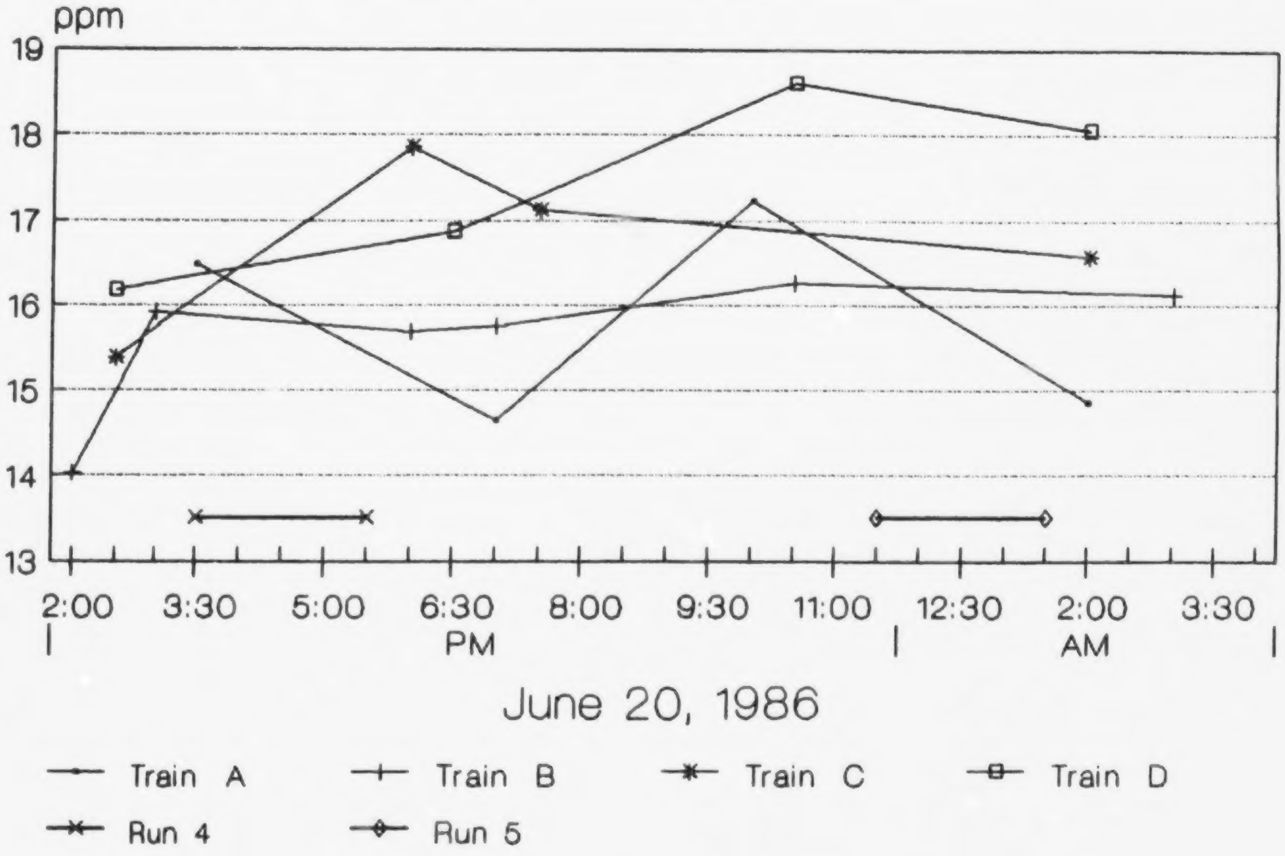


Figure C-30. Concentration vs time.

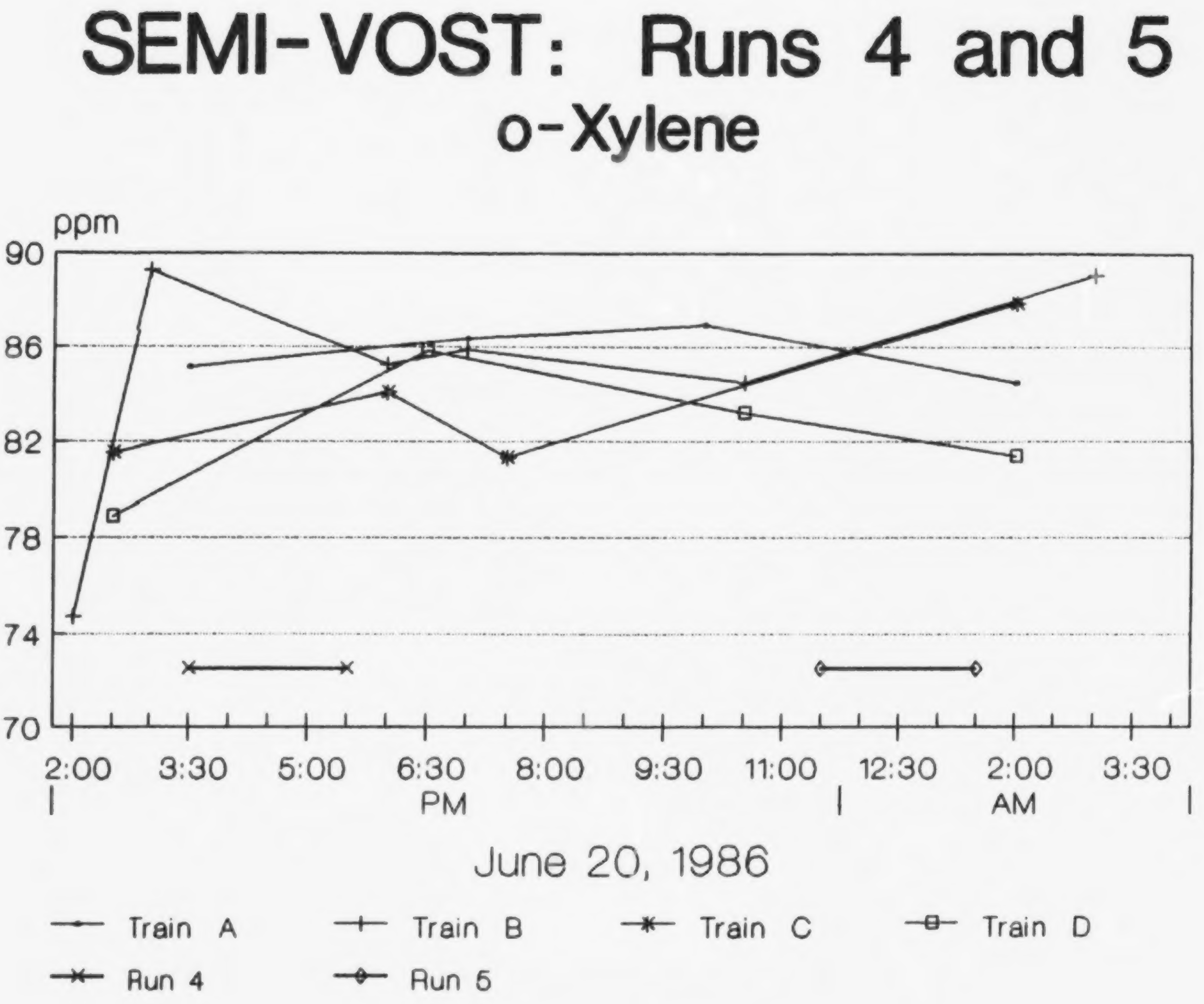


Figure C-31. Concentration vs time.

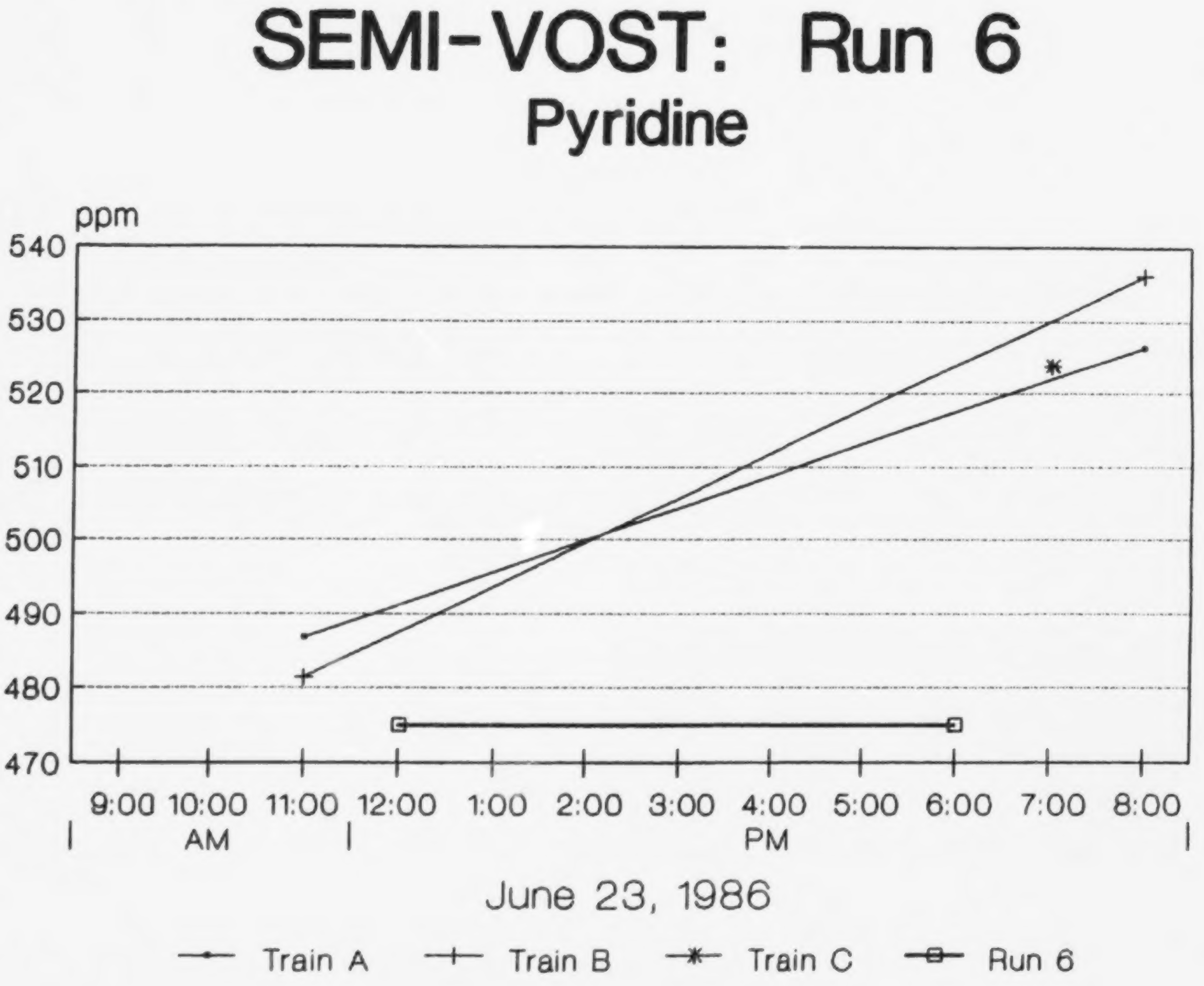


Figure C-32. Concentration vs time.

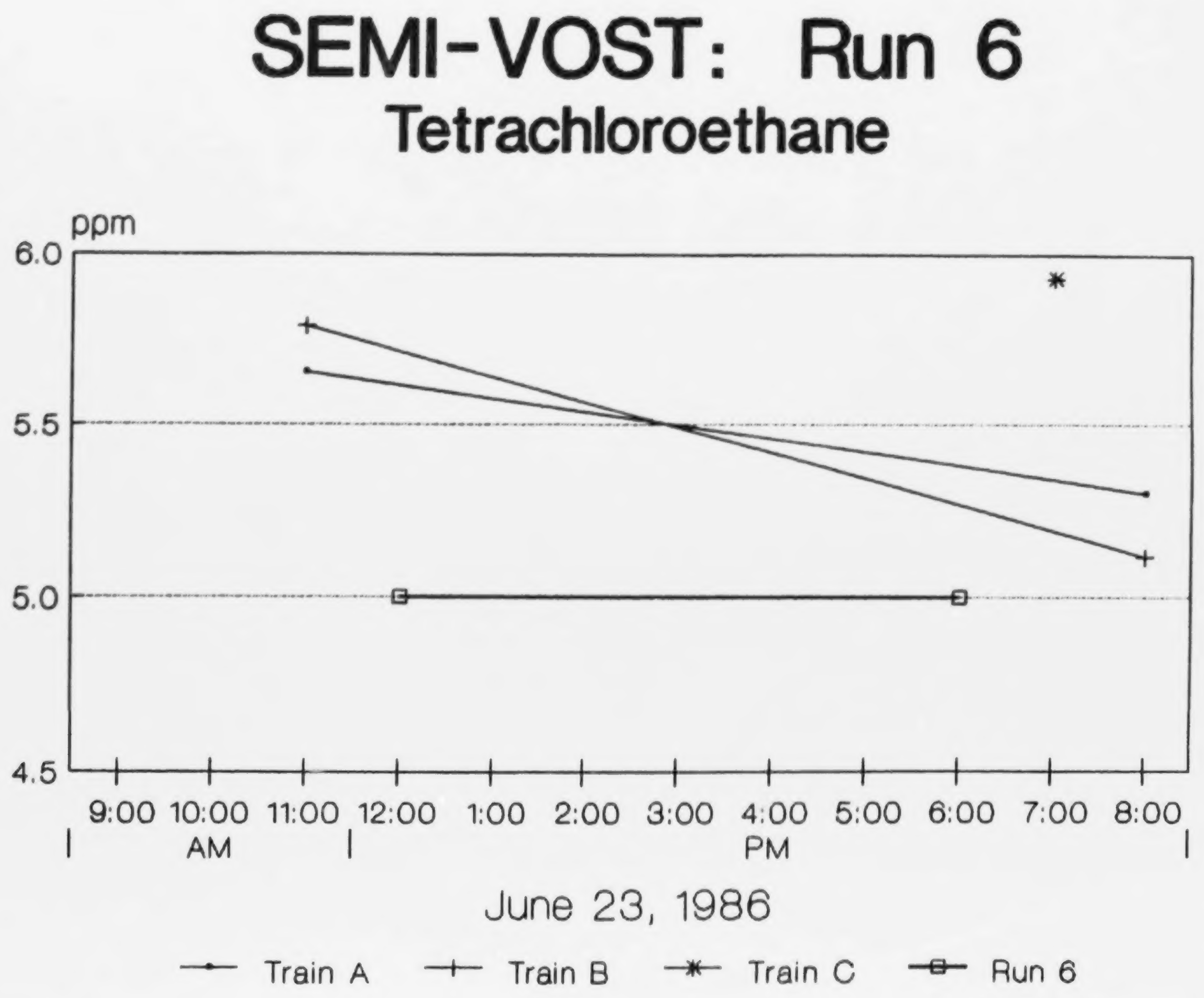


Figure C-33. Concentration vs time.

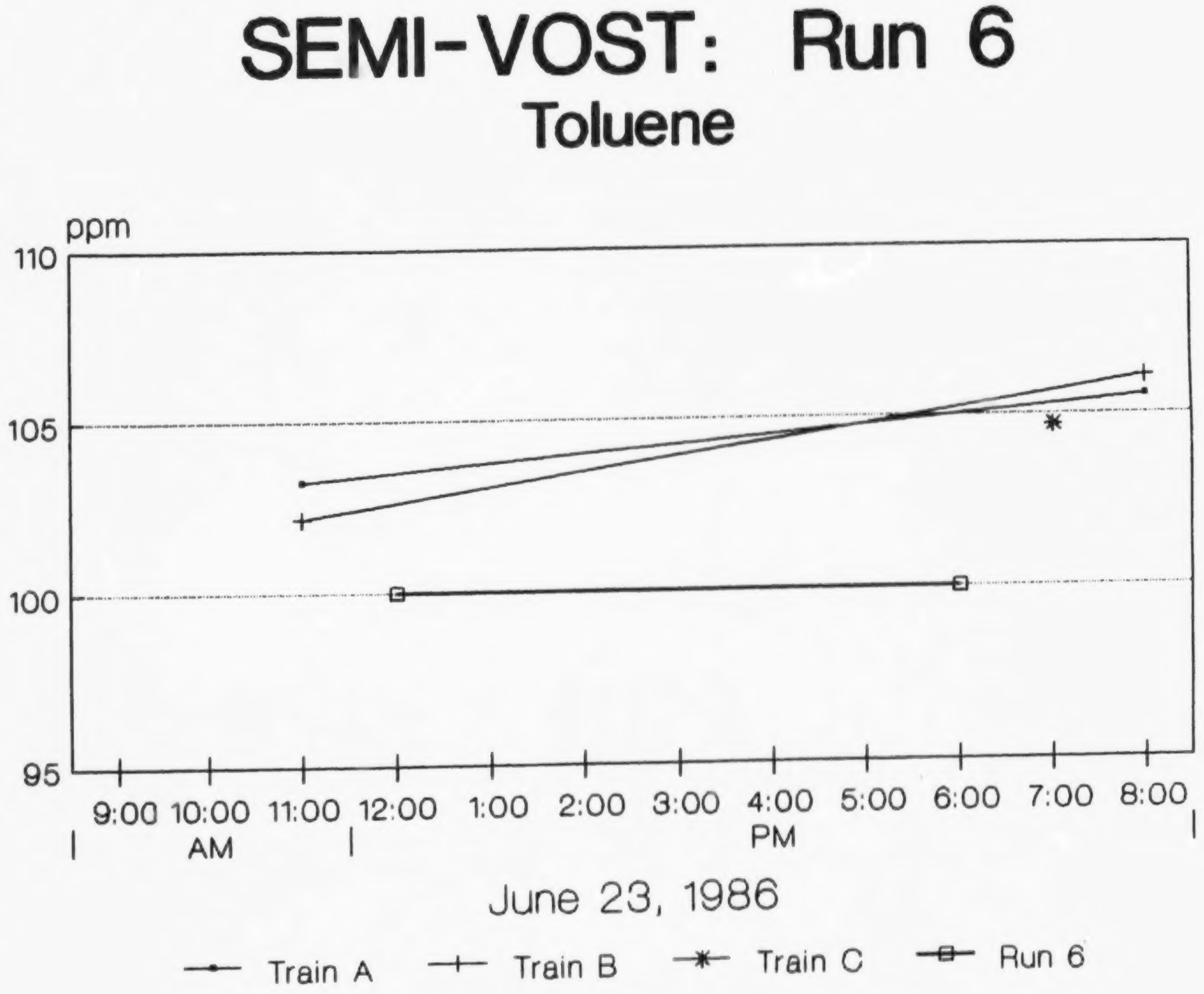


Figure C-34. Concentration vs time.

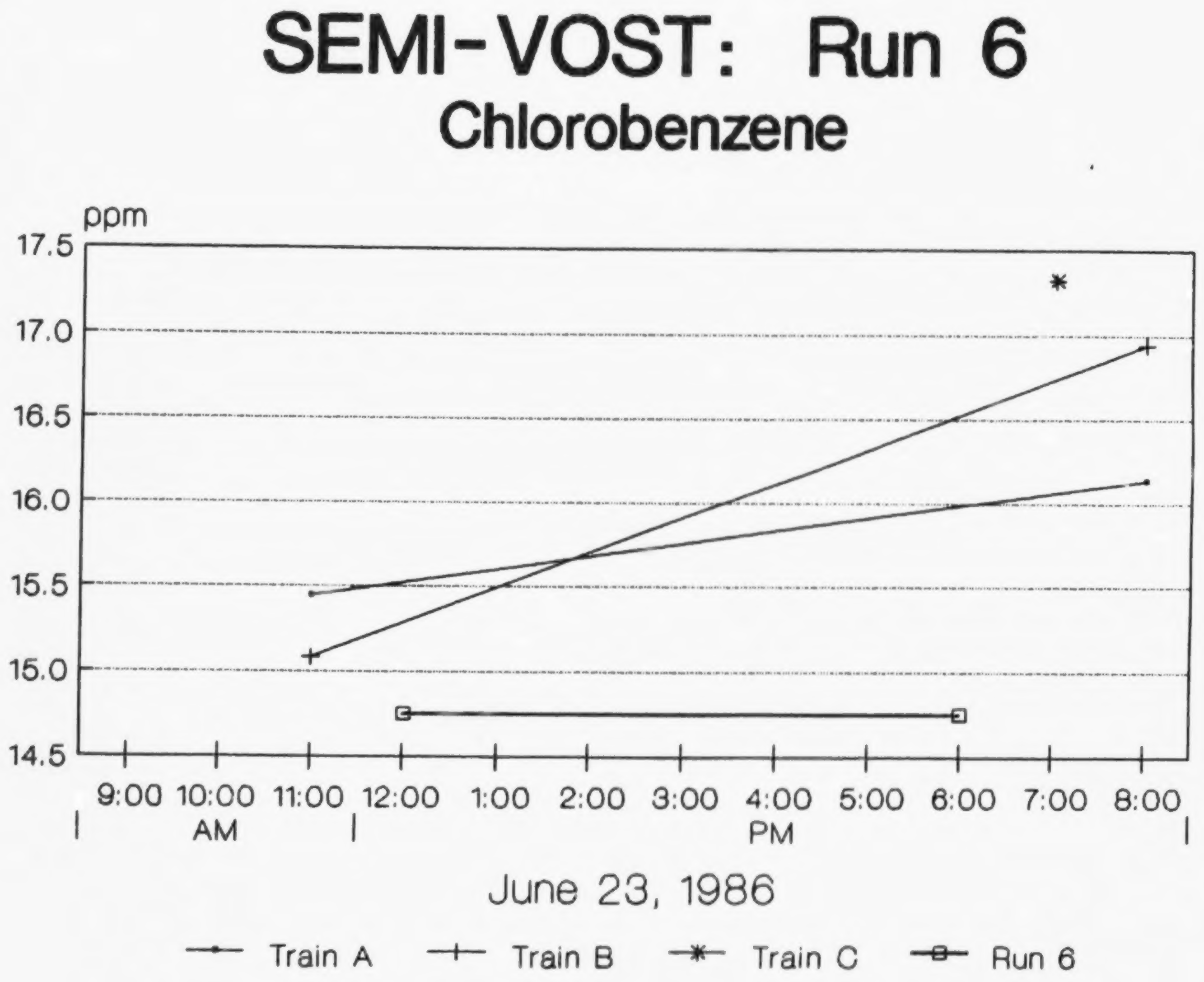


Figure C-35. Concentration vs time.

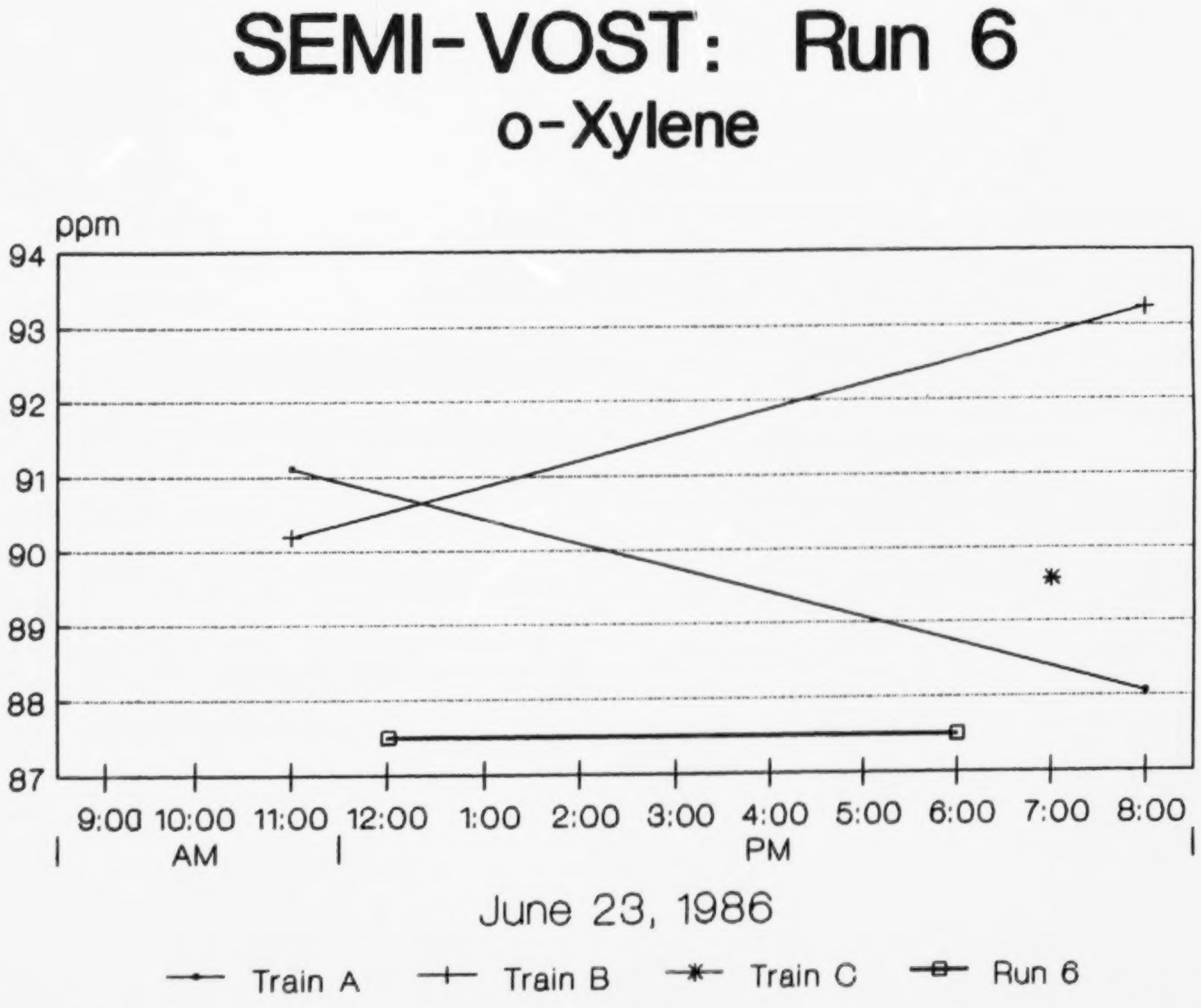
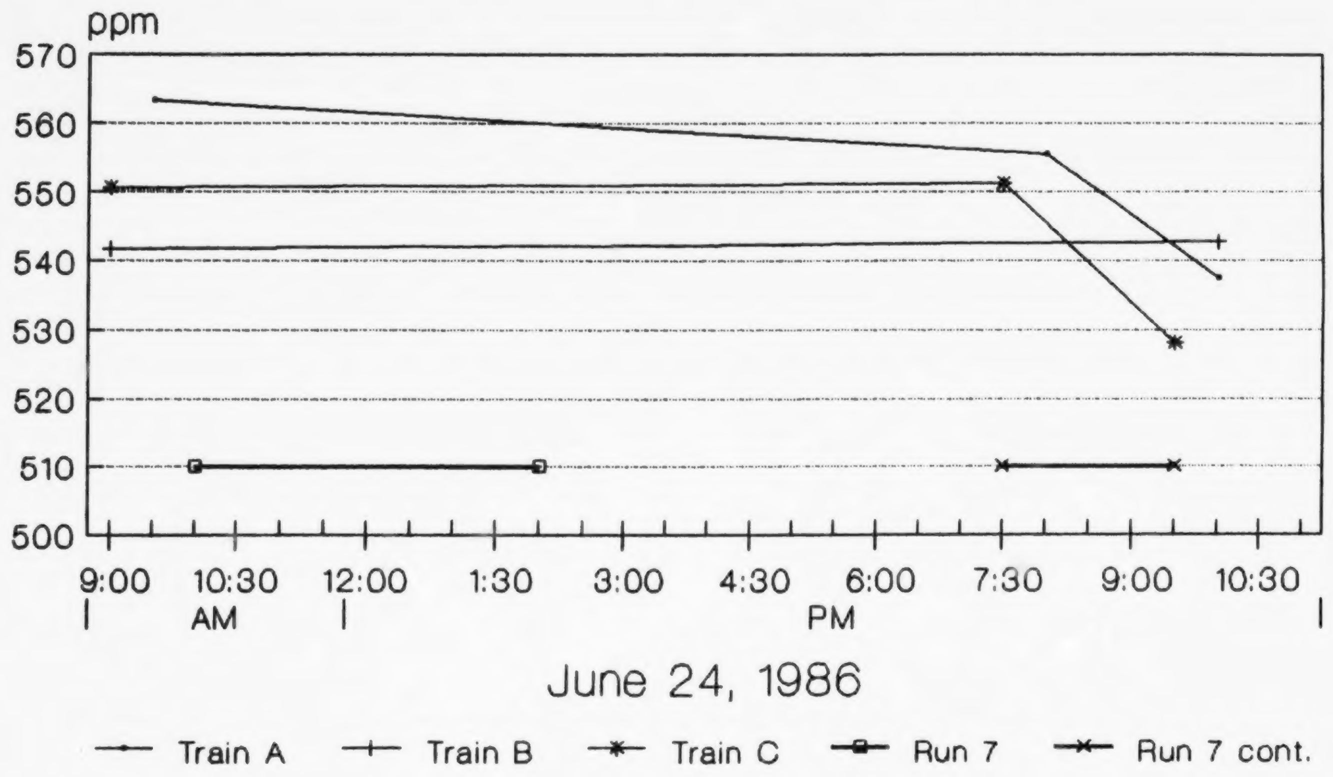


Figure C-36. Concentration vs time.

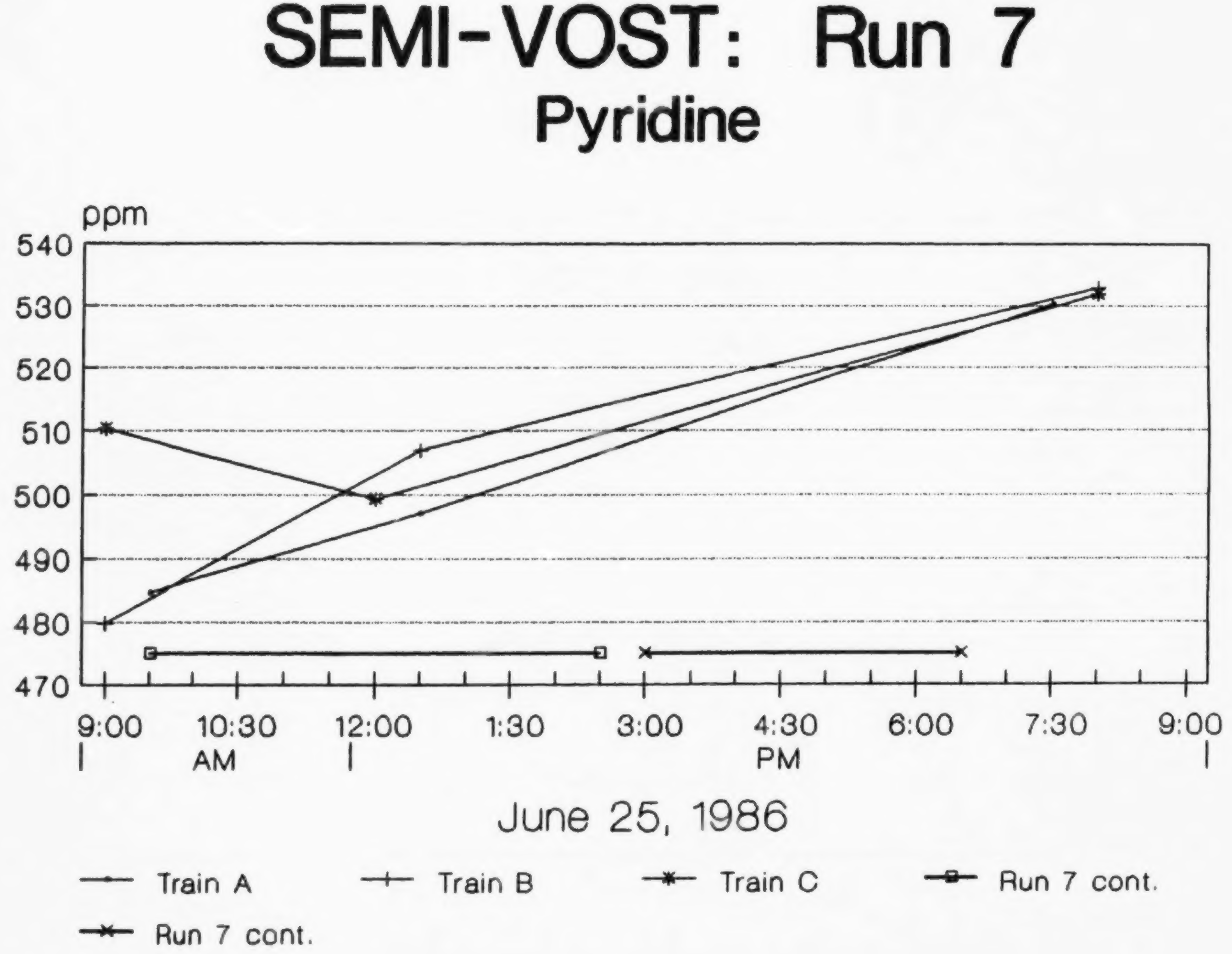
SEMI-VOST: Run 7

Pyridine



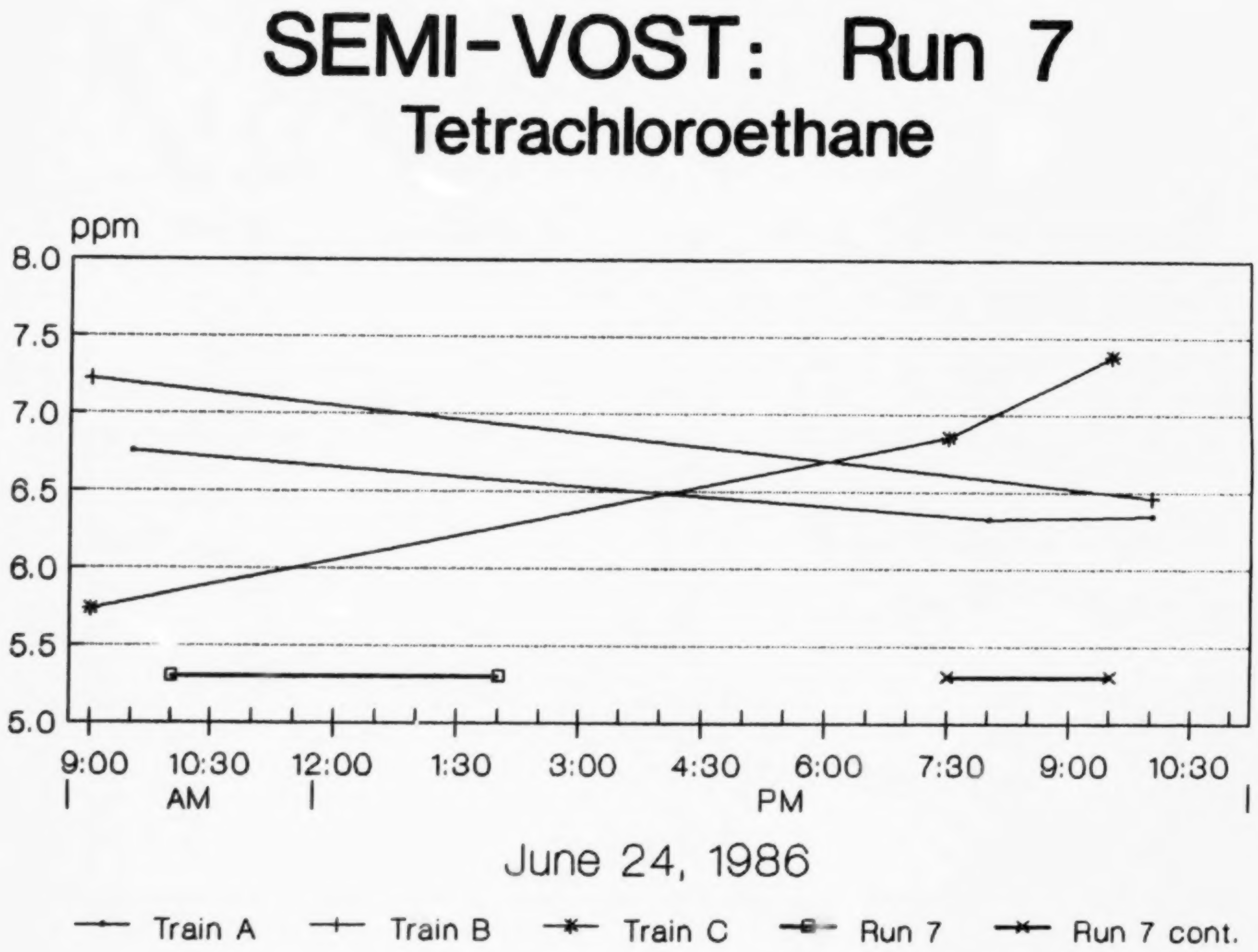
Day 1

Figure C-37. Concentration vs time.



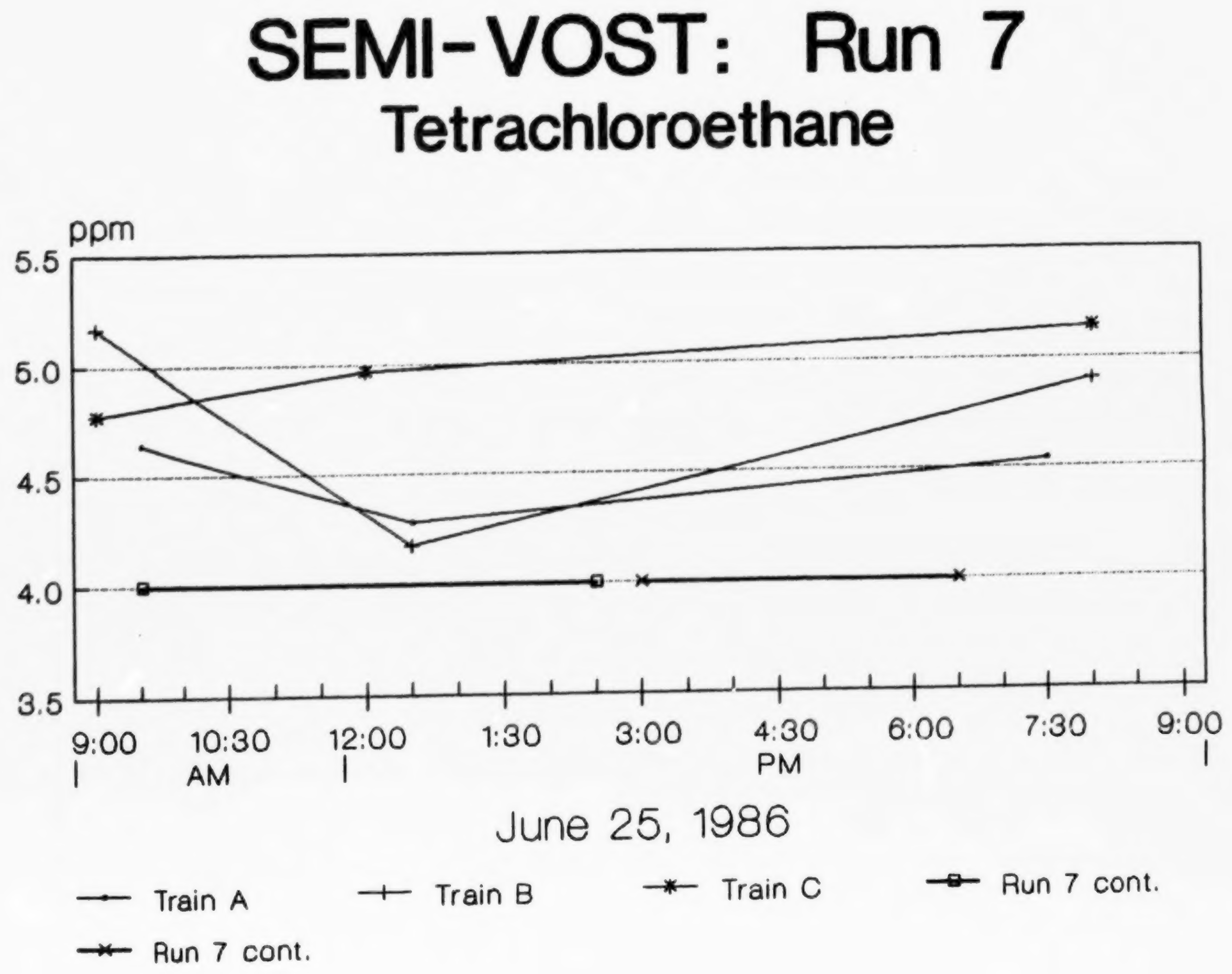
Day 2

Figure C-38. Concentration vs time.



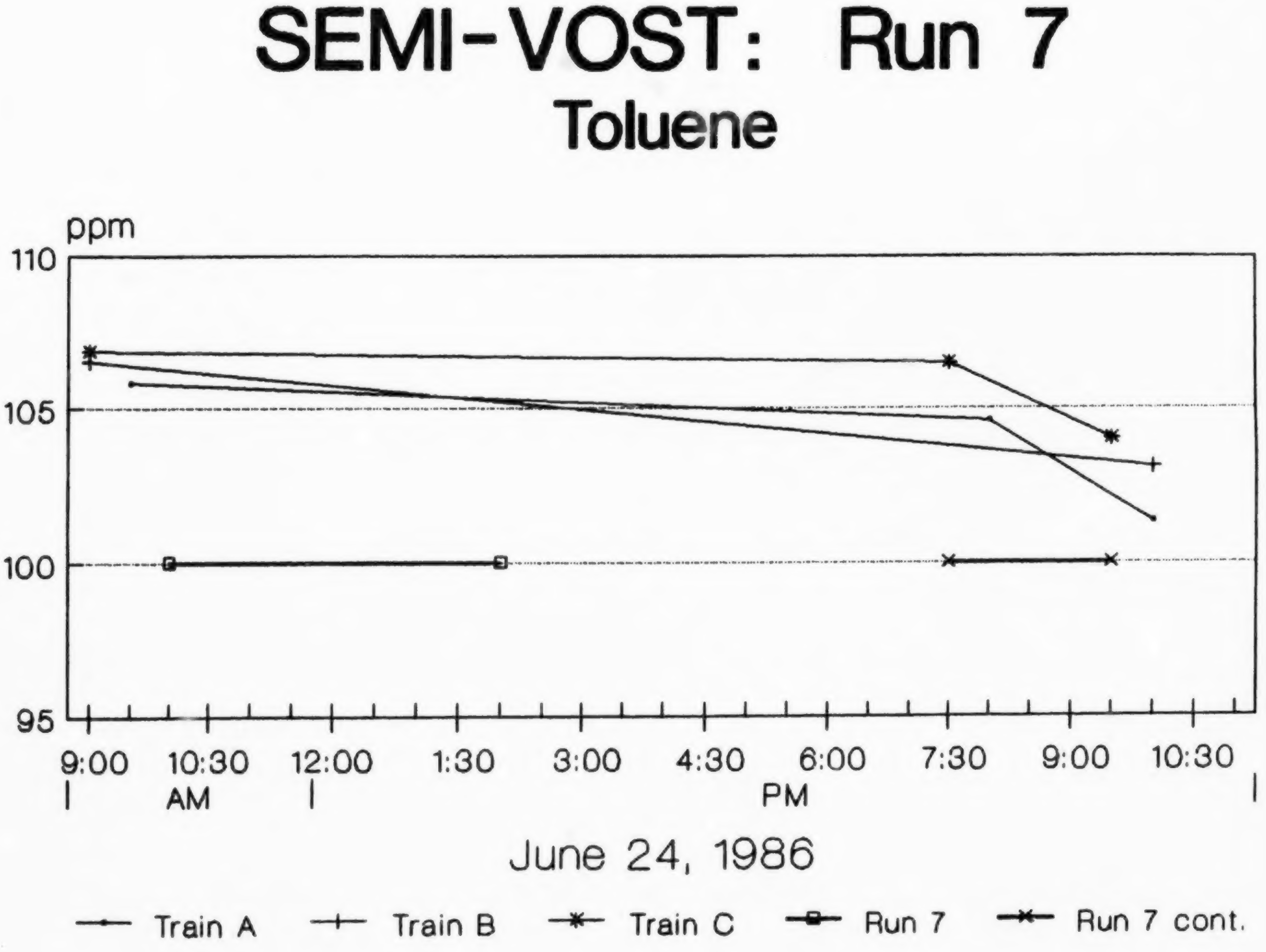
Day 1

Figure C-39. Concentration vs time.



Day 2

Figure C-40. Concentration vs time.

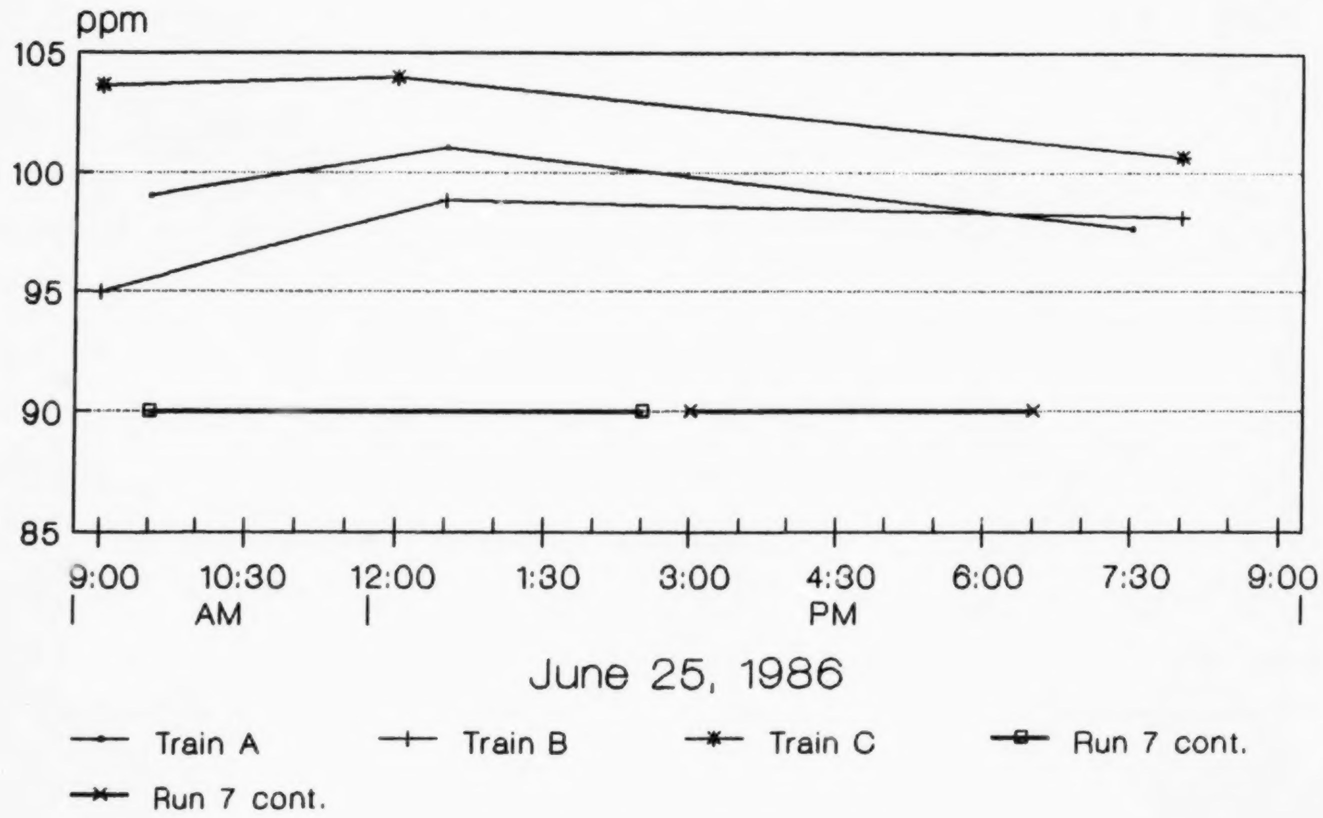

SEMI-VOST: Run 7
Toluene

Day 1

Figure C-41. Concentration vs time.

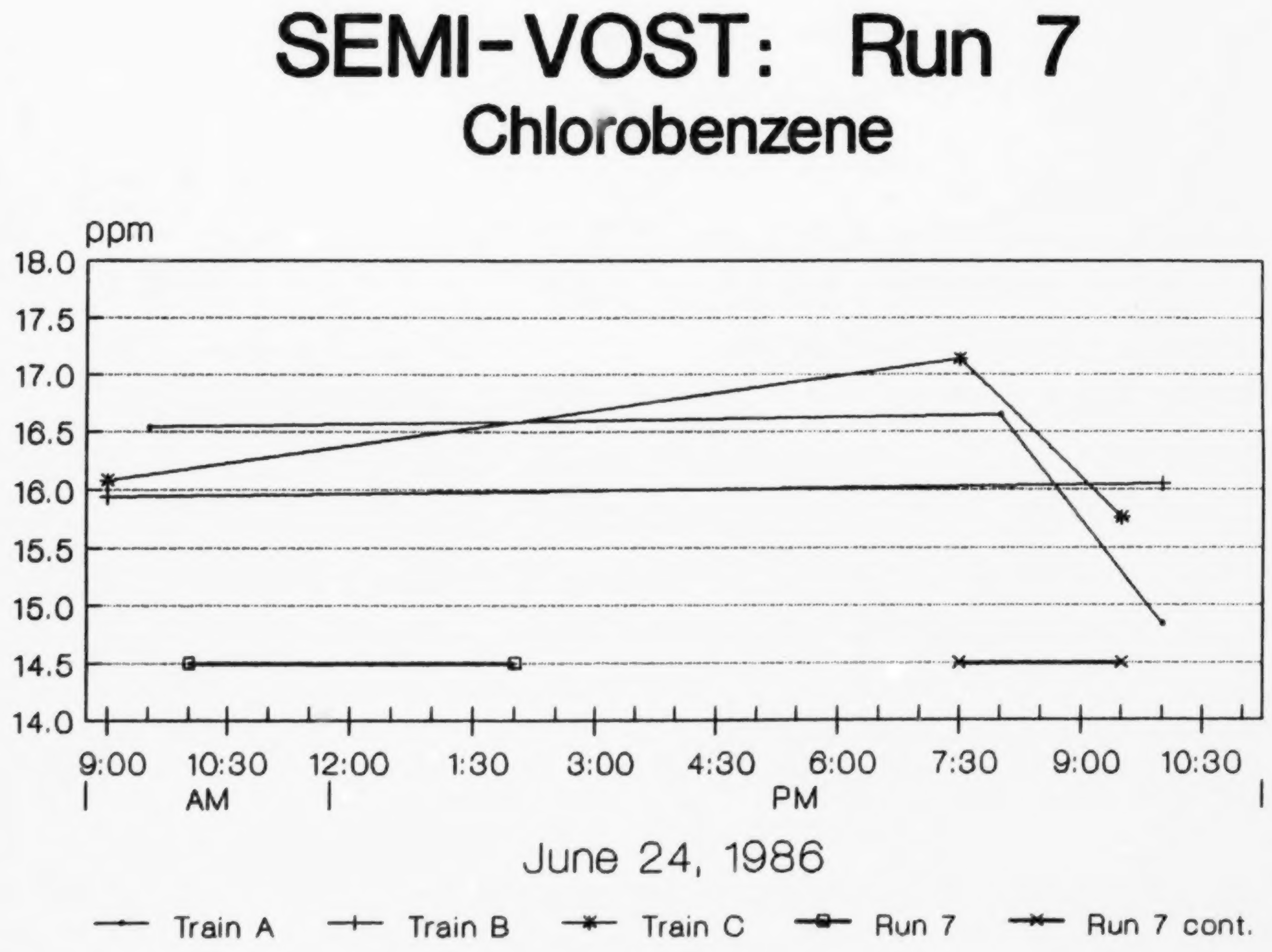
SEMI-VOST: Run 7

Toluene



Day 2

Figure C-42. Concentration vs time.

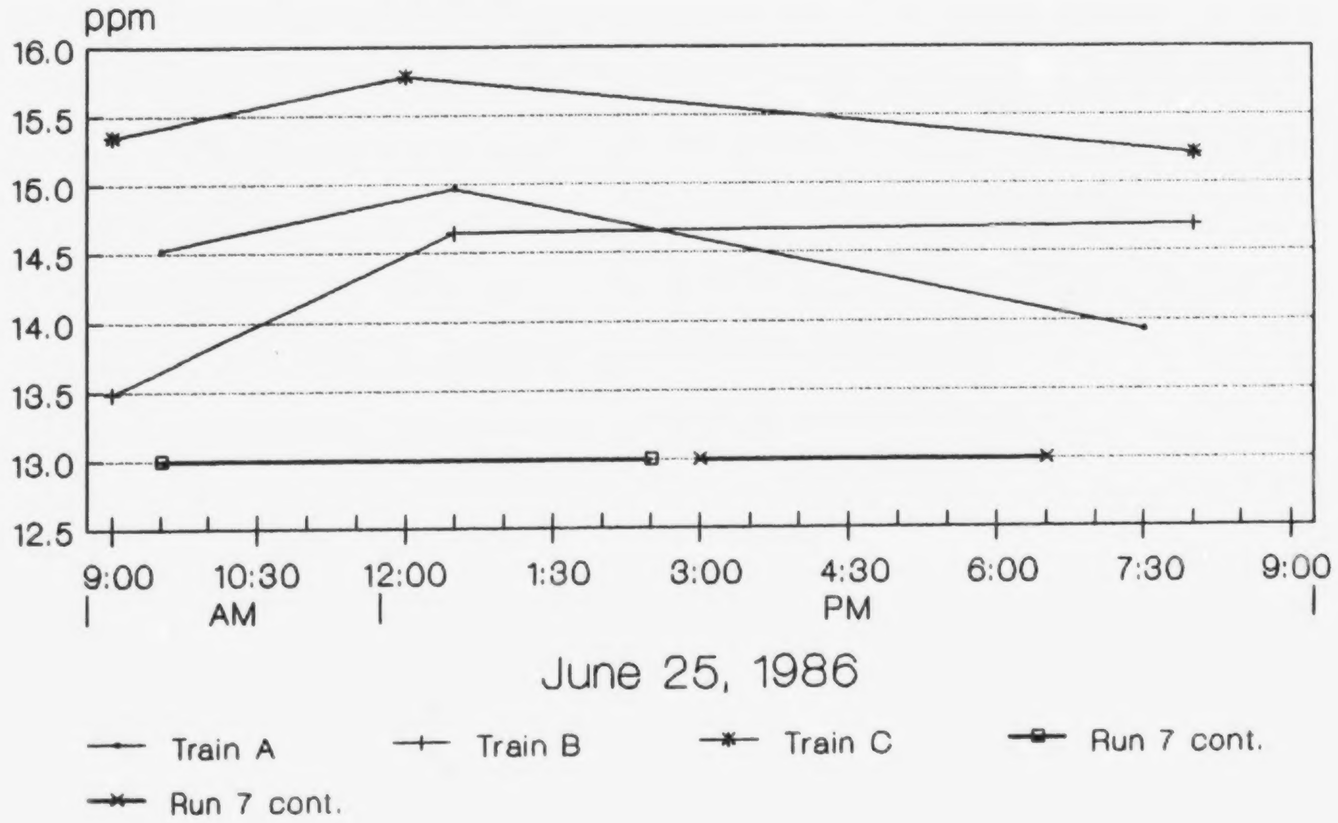


Day 1

Figure C-43. Concentration vs time.

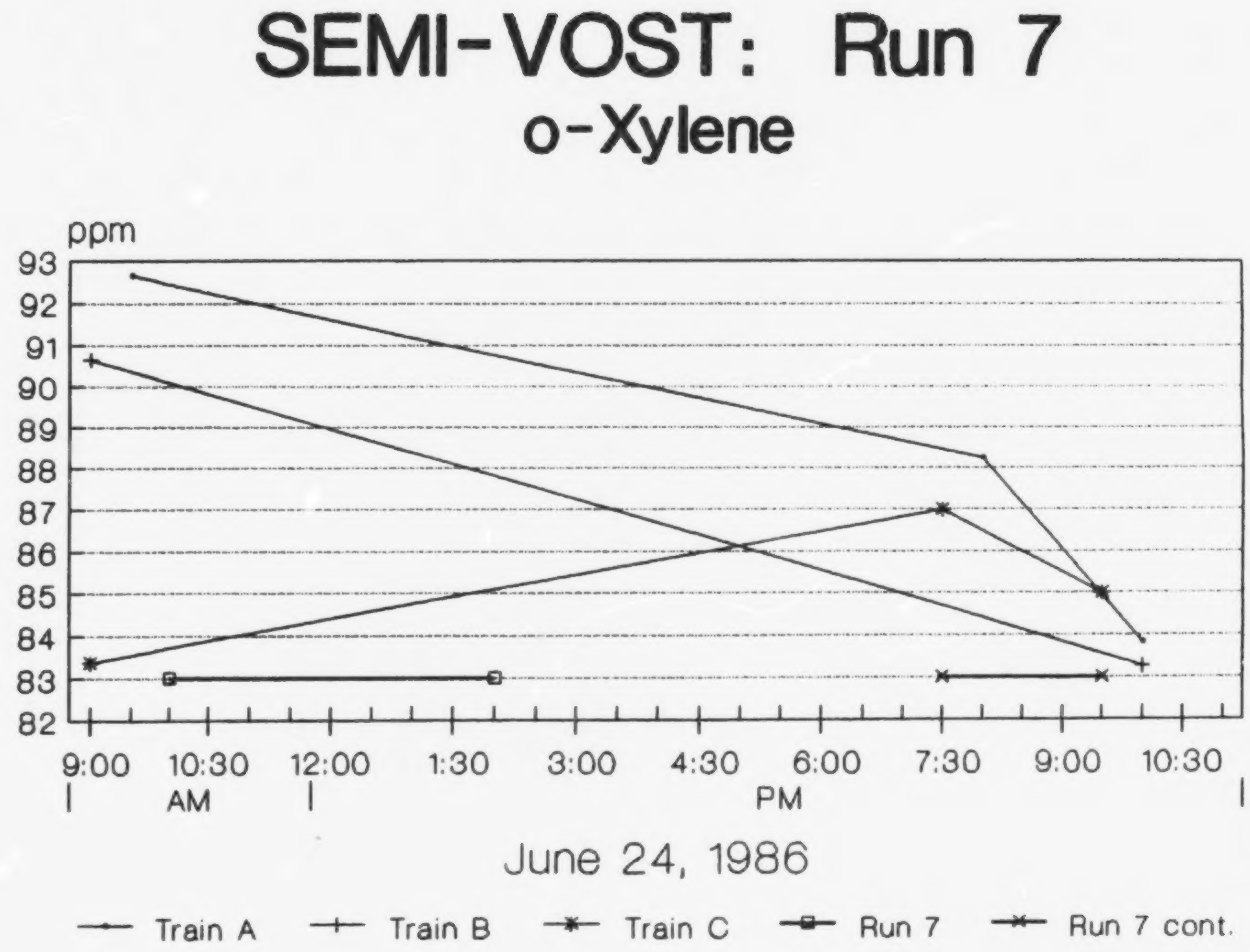
SEMI-VOST: Run 7

Chlorobenzene



Day 2

Figure C-44. Concentration vs time.

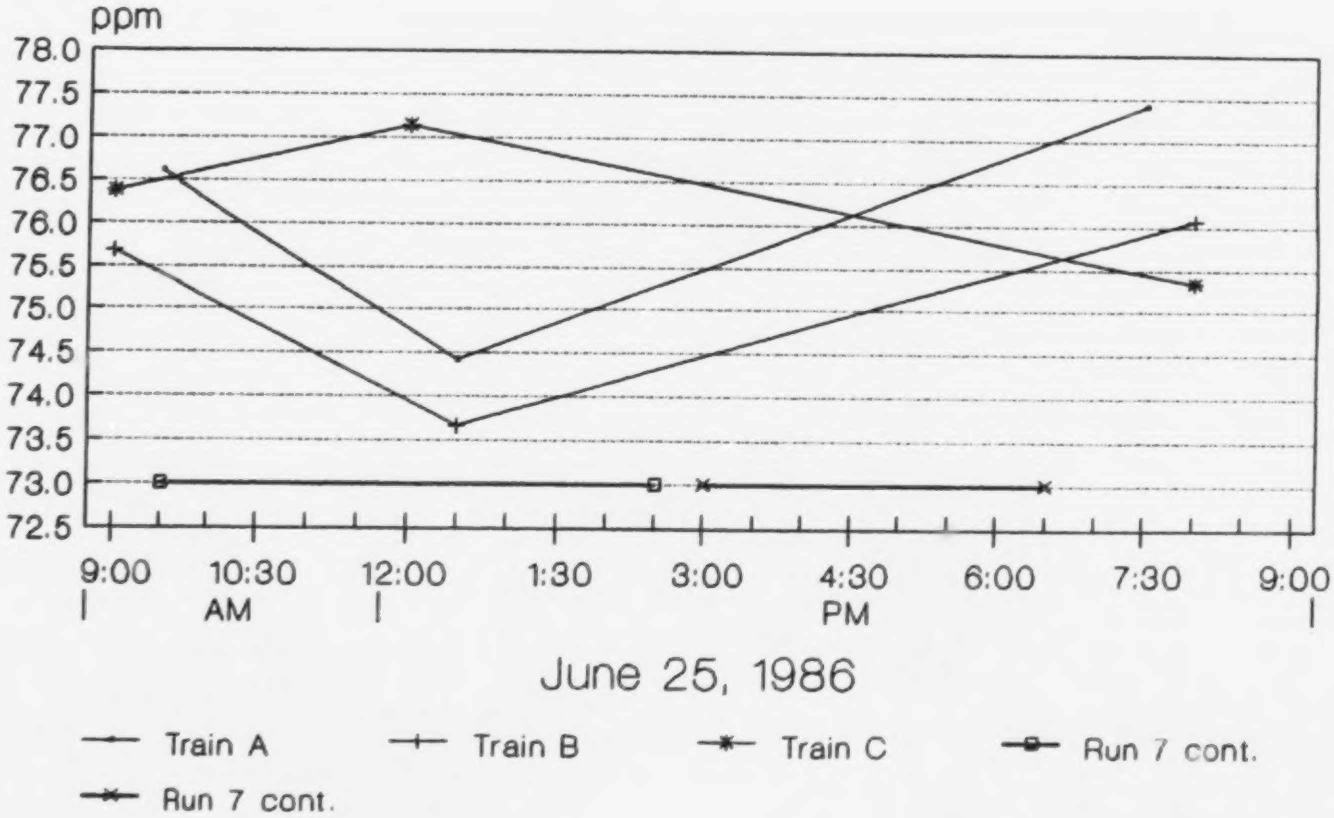


Day 1

Figure C-45. Concentration vs time.

SEMI-VOST: Run 7

o-Xylene



June 25, 1986

Day 2

Figure C-46. Concentration vs time.

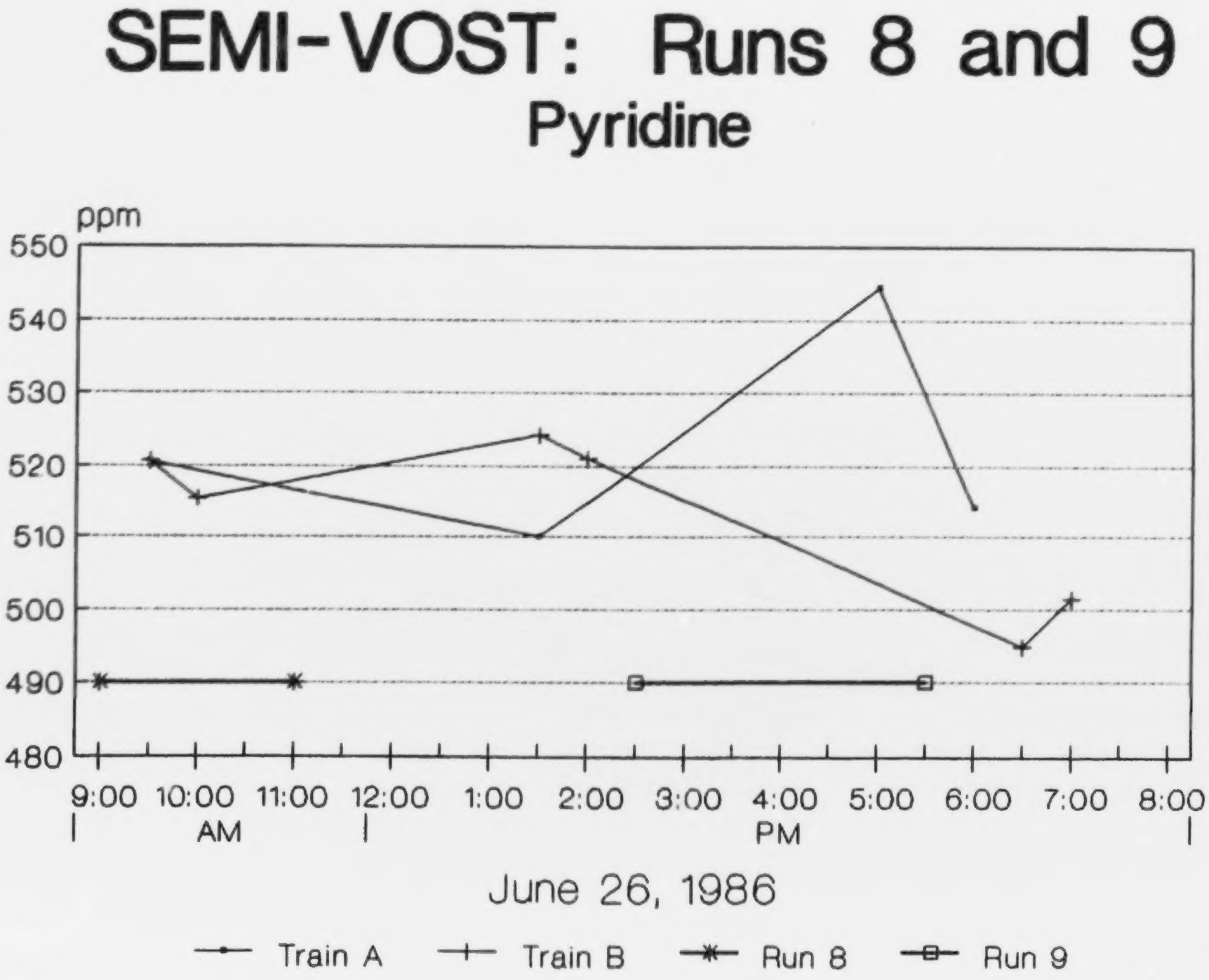


Figure C-47. Concentration vs time.

SEMI-VOST: Runs 8 and 9

Tetrachloroethane

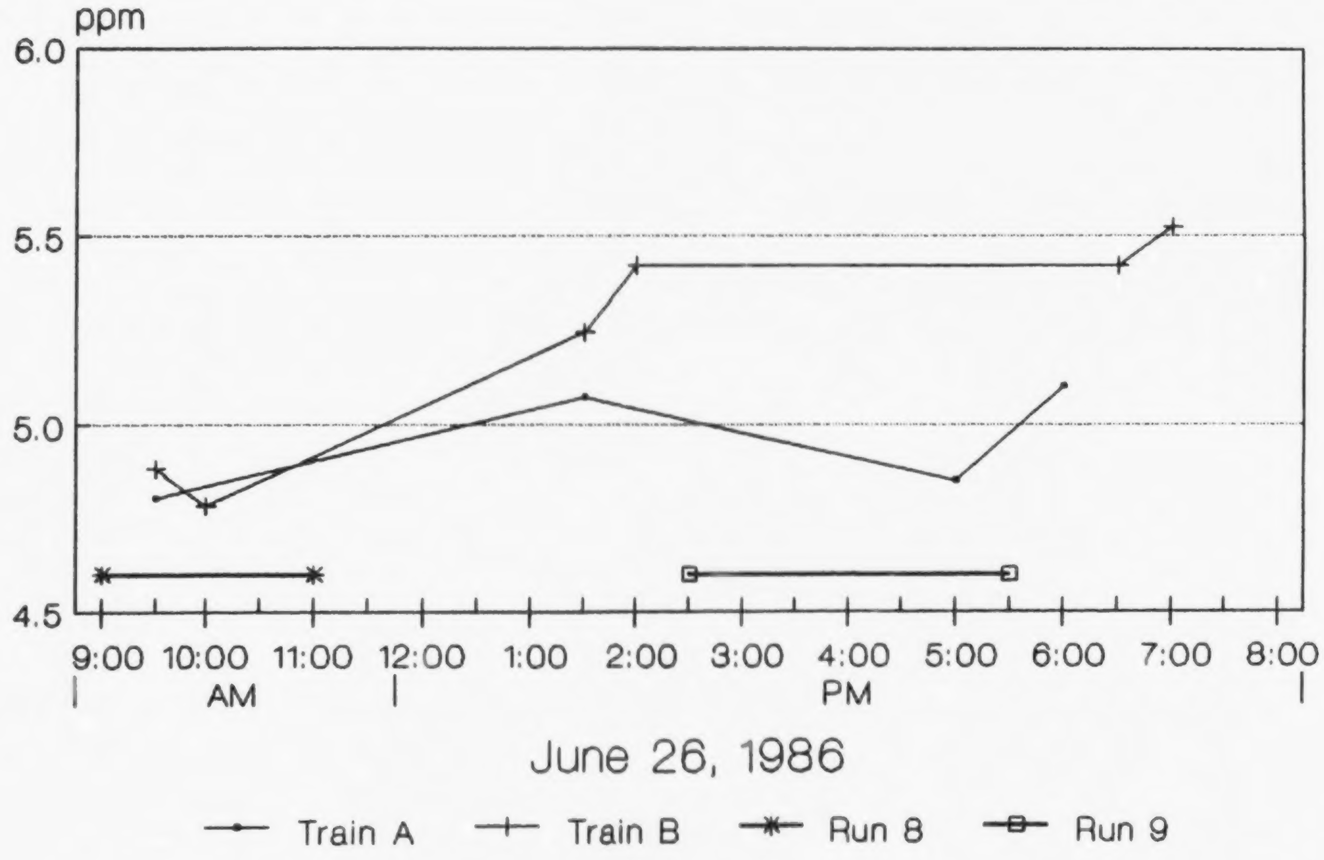


Figure C-48. Concentration vs time.

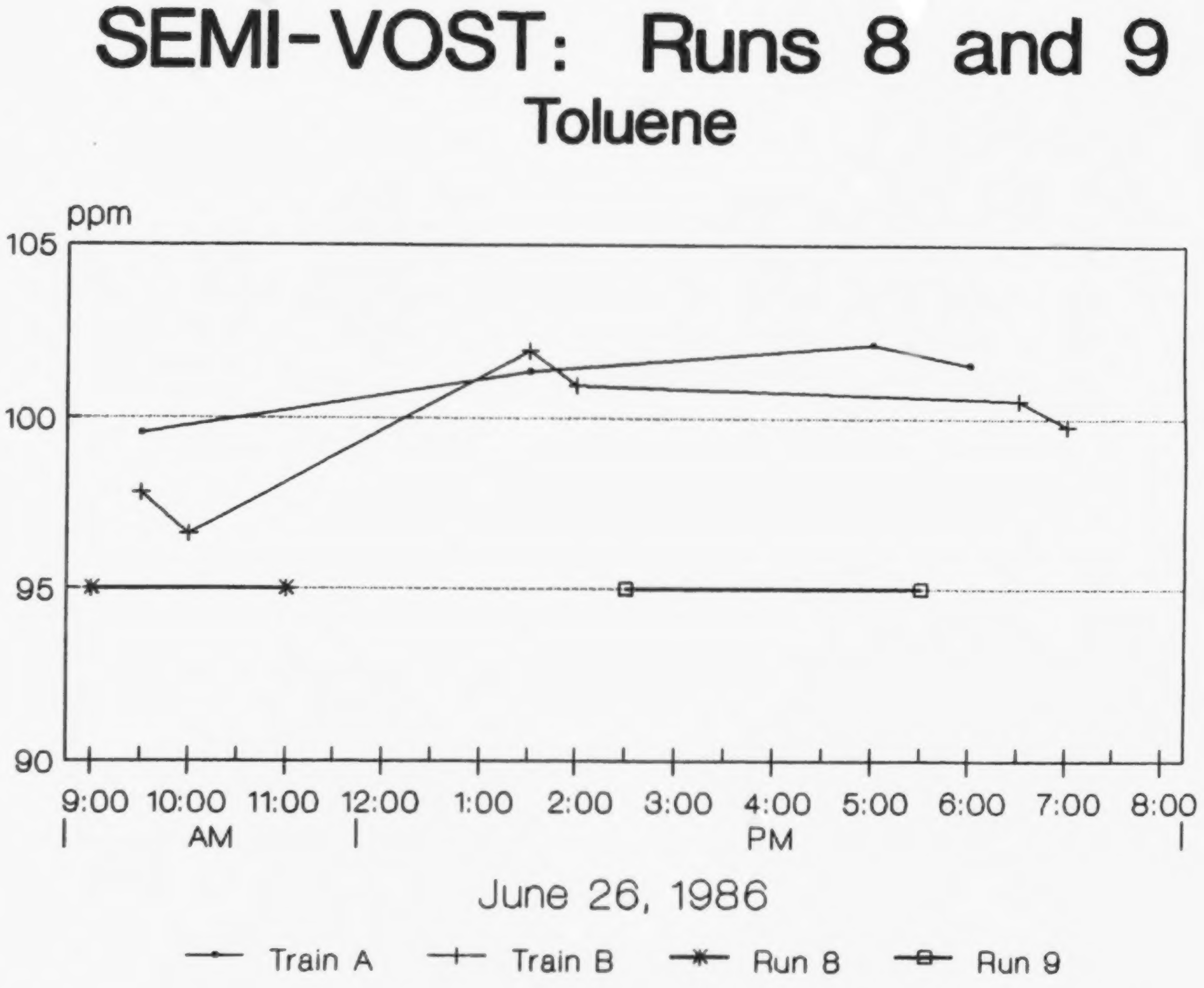


Figure C-49. Concentration vs time.

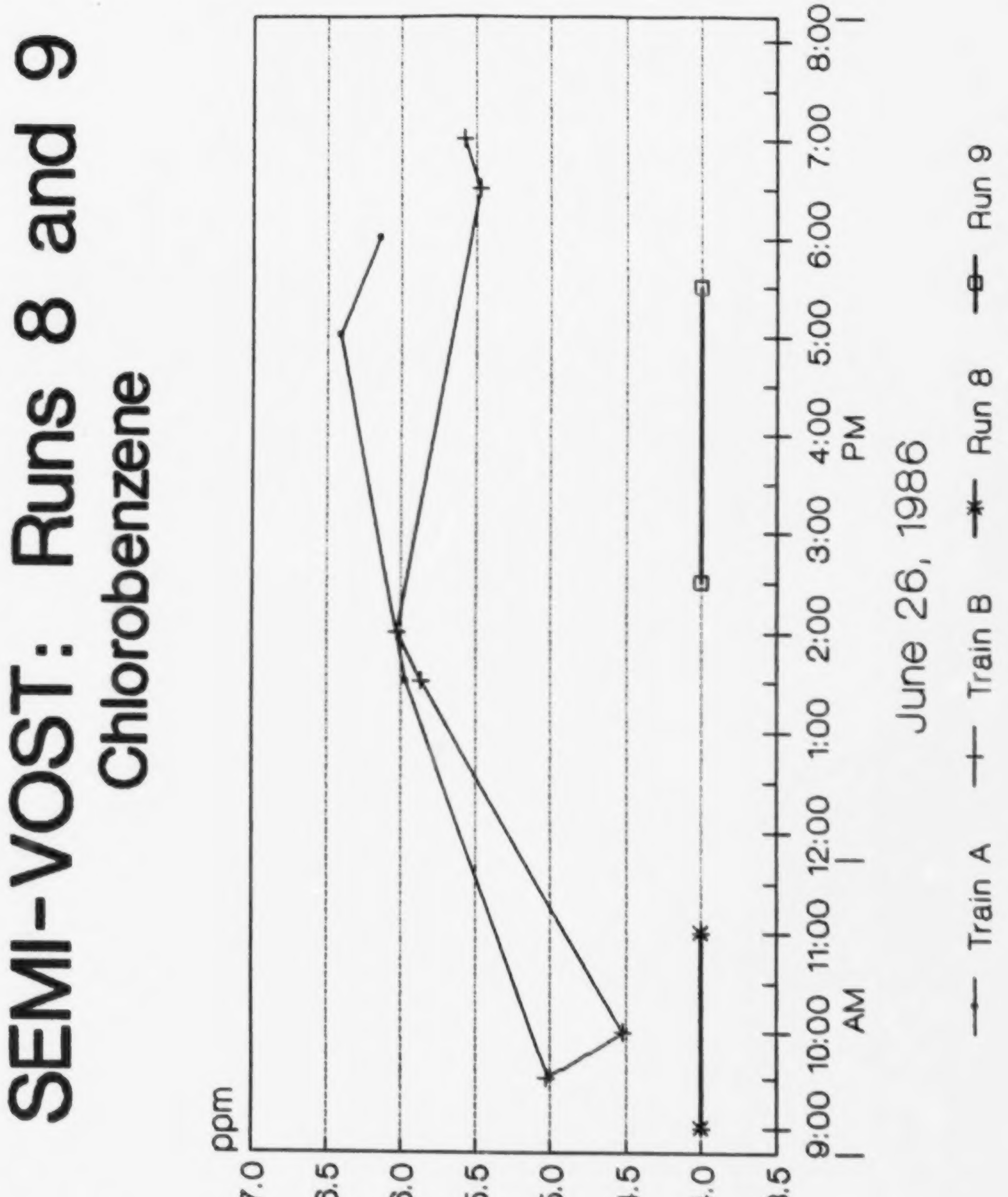


Figure C-50. Concentration vs time.

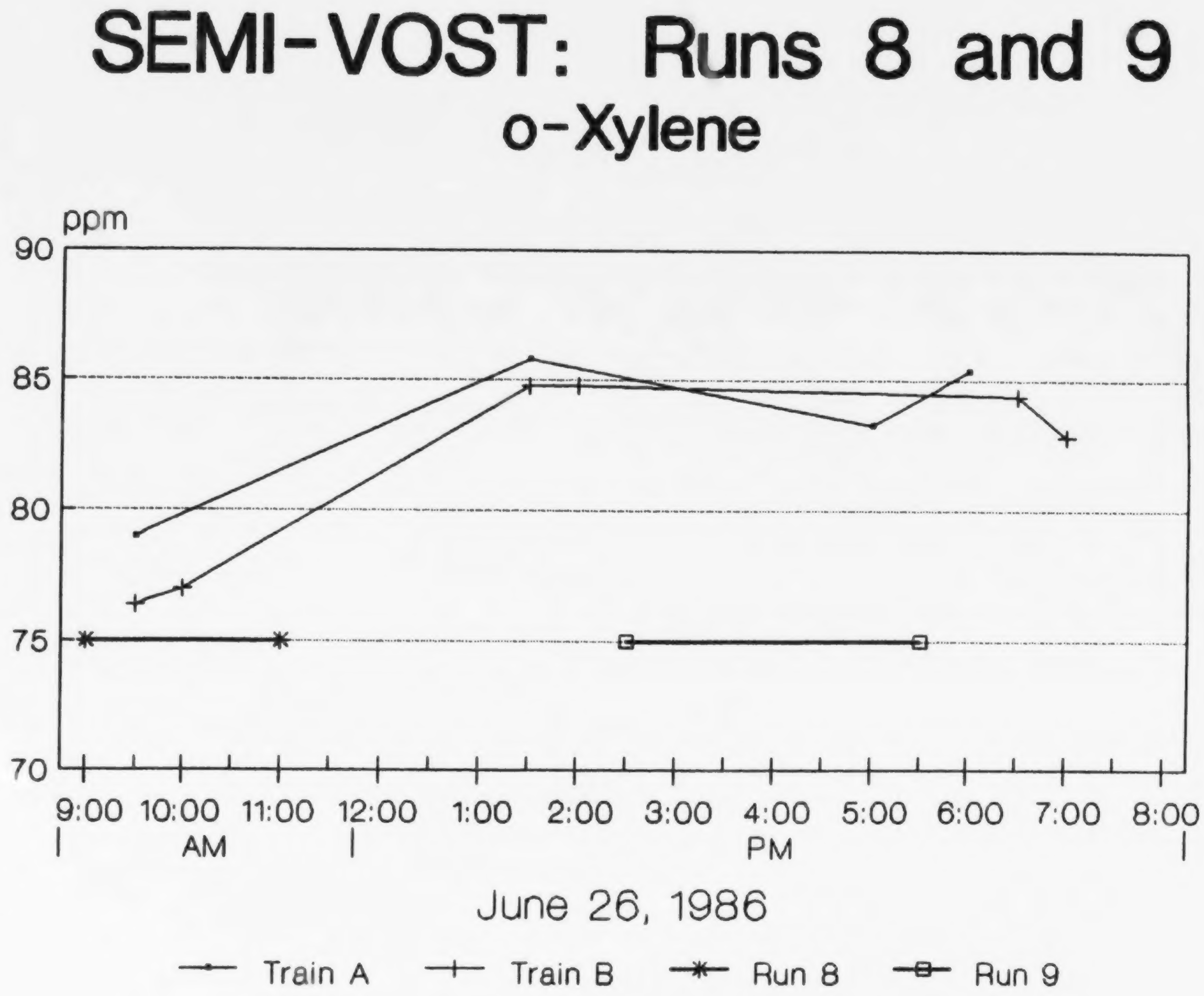


Figure C-51. Concentration vs time.

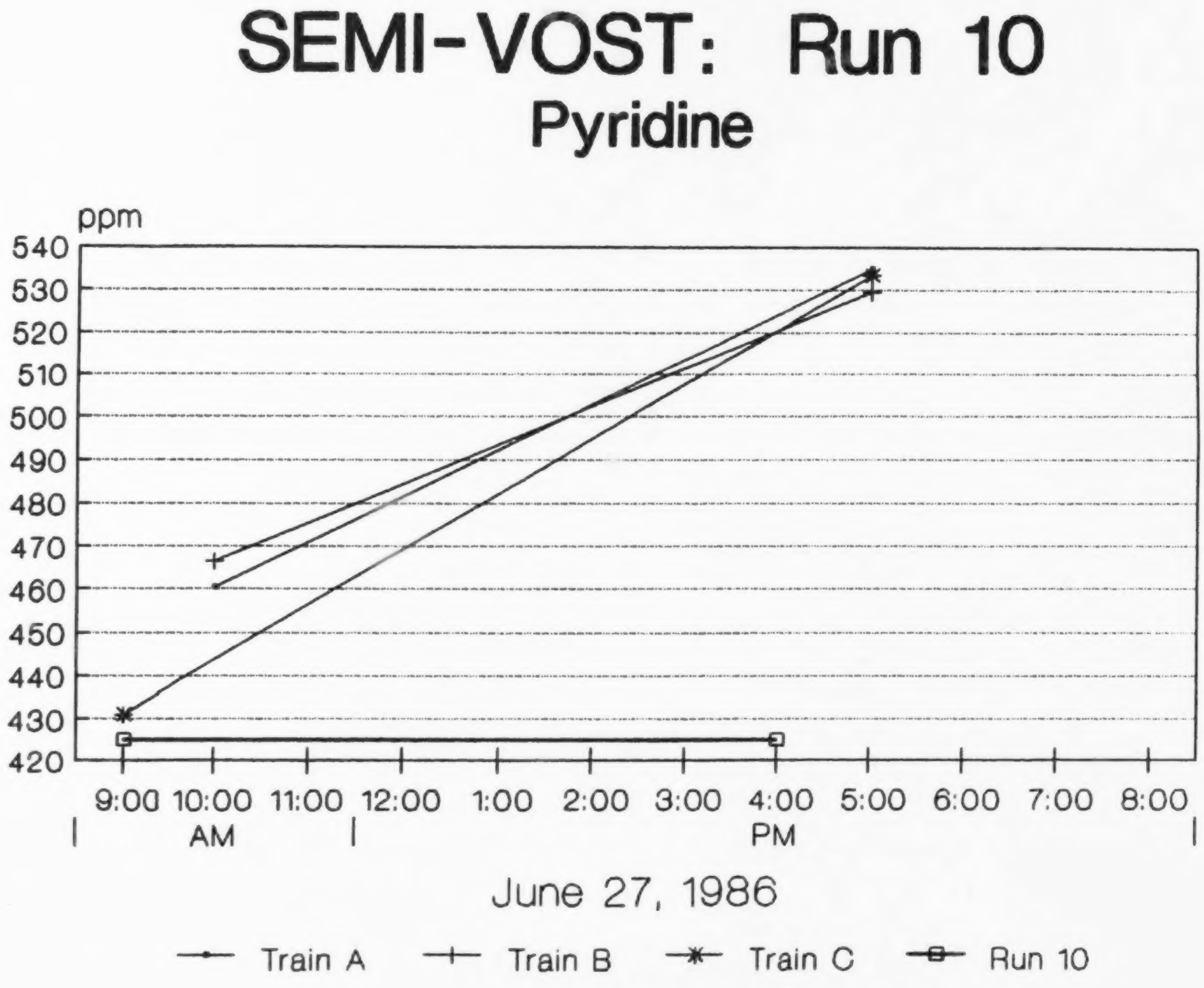


Figure C-52. Concentration vs time.

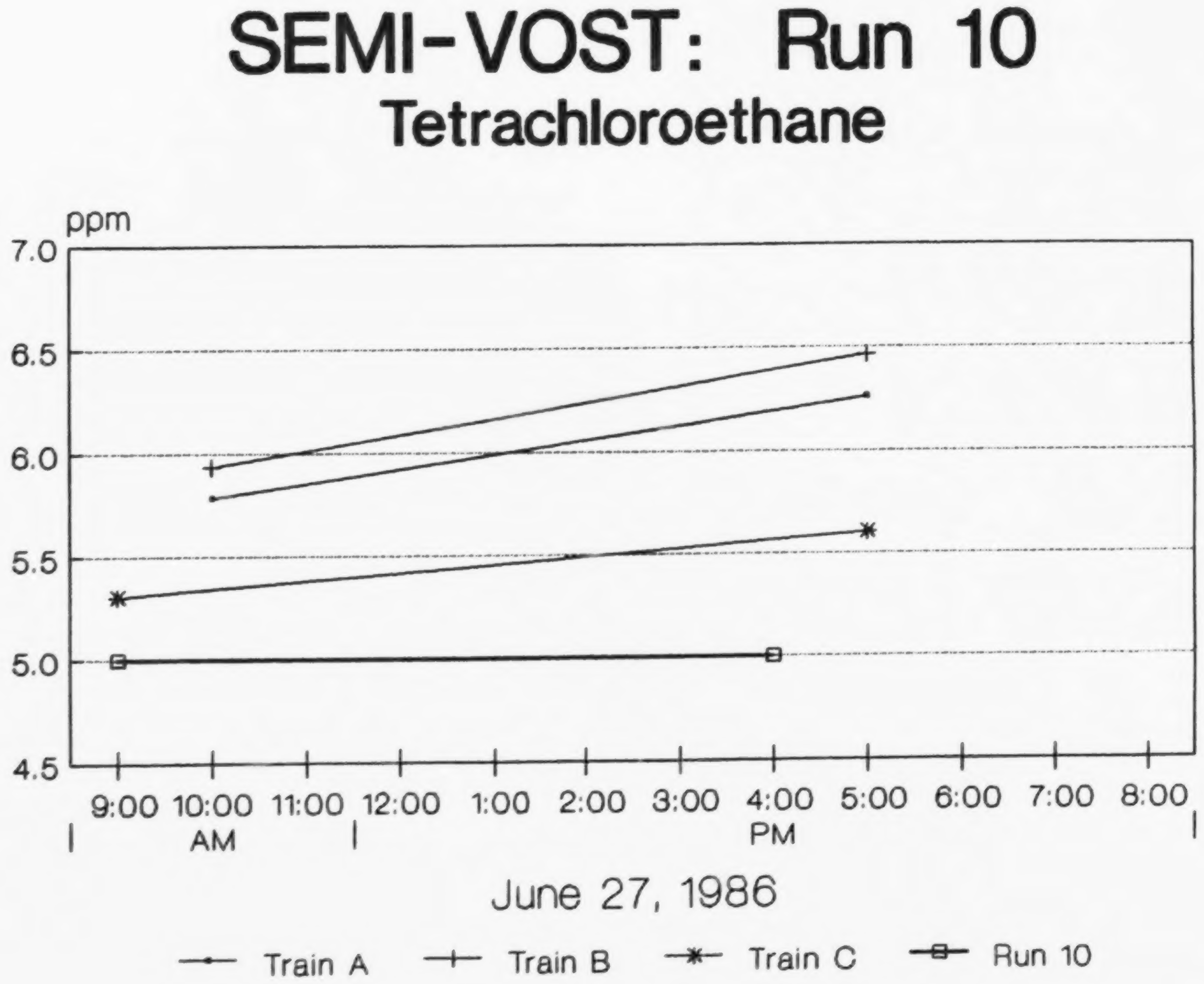


Figure C-53. Concentration vs time.

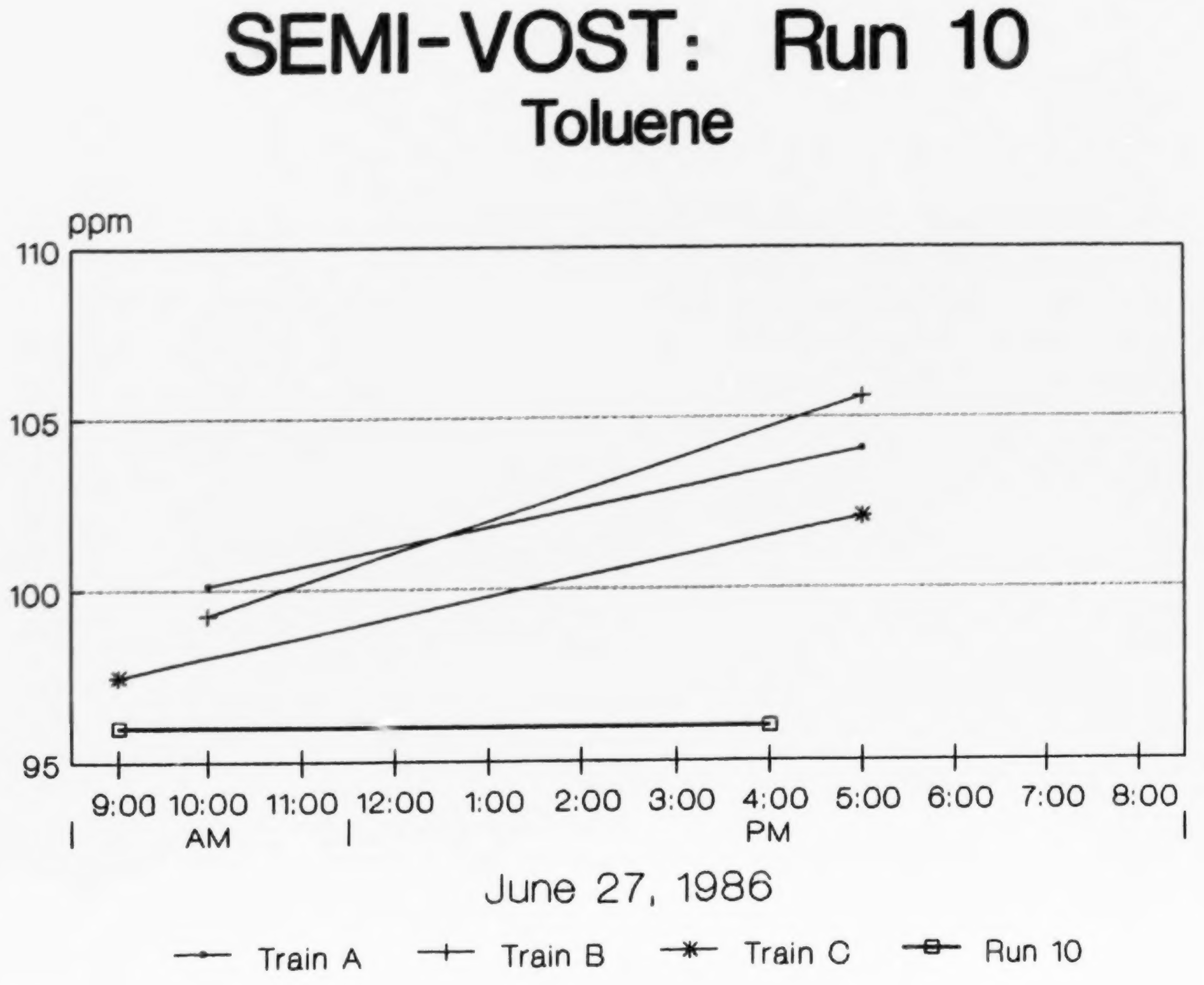


Figure C-54. Concentration vs time.

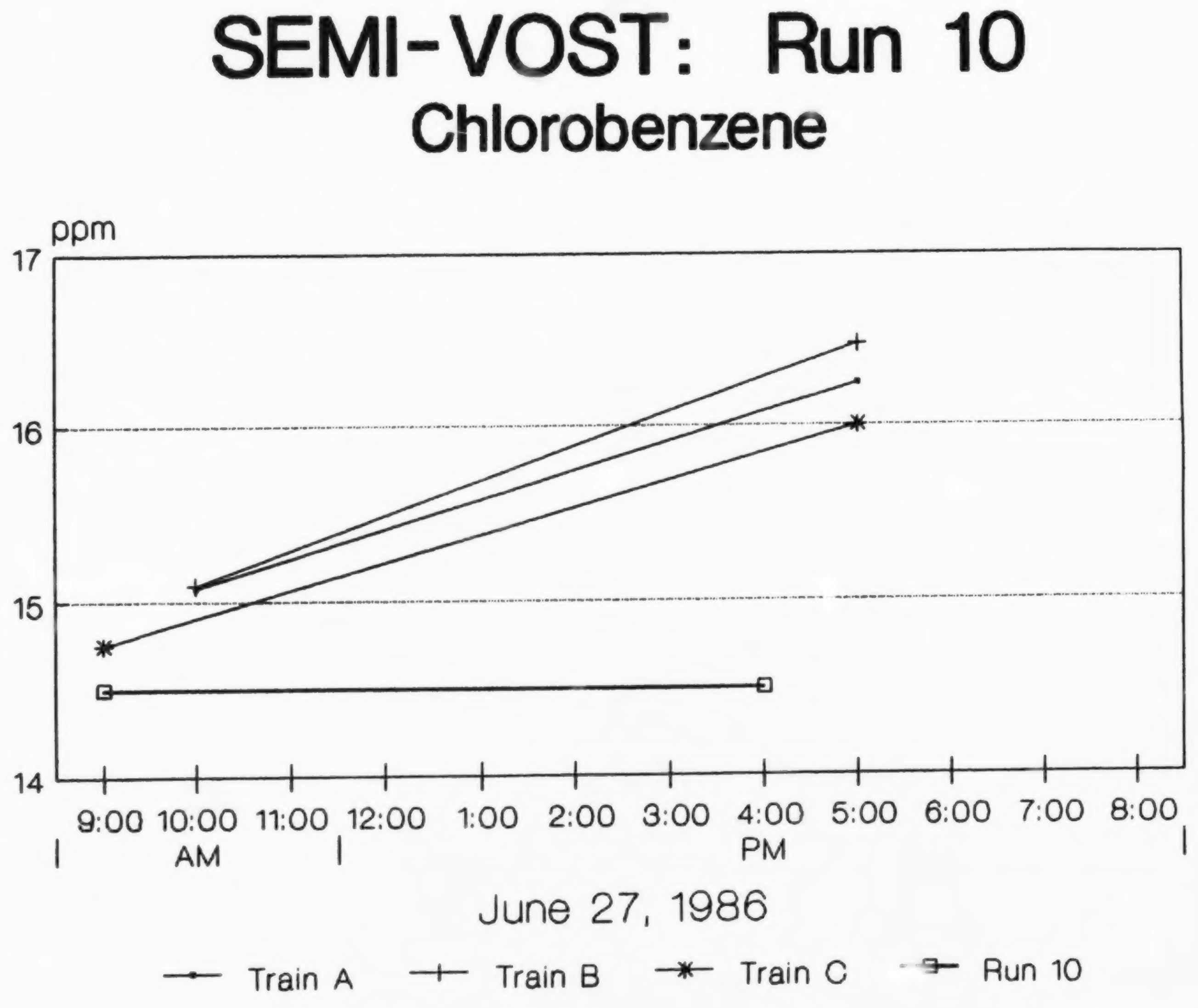
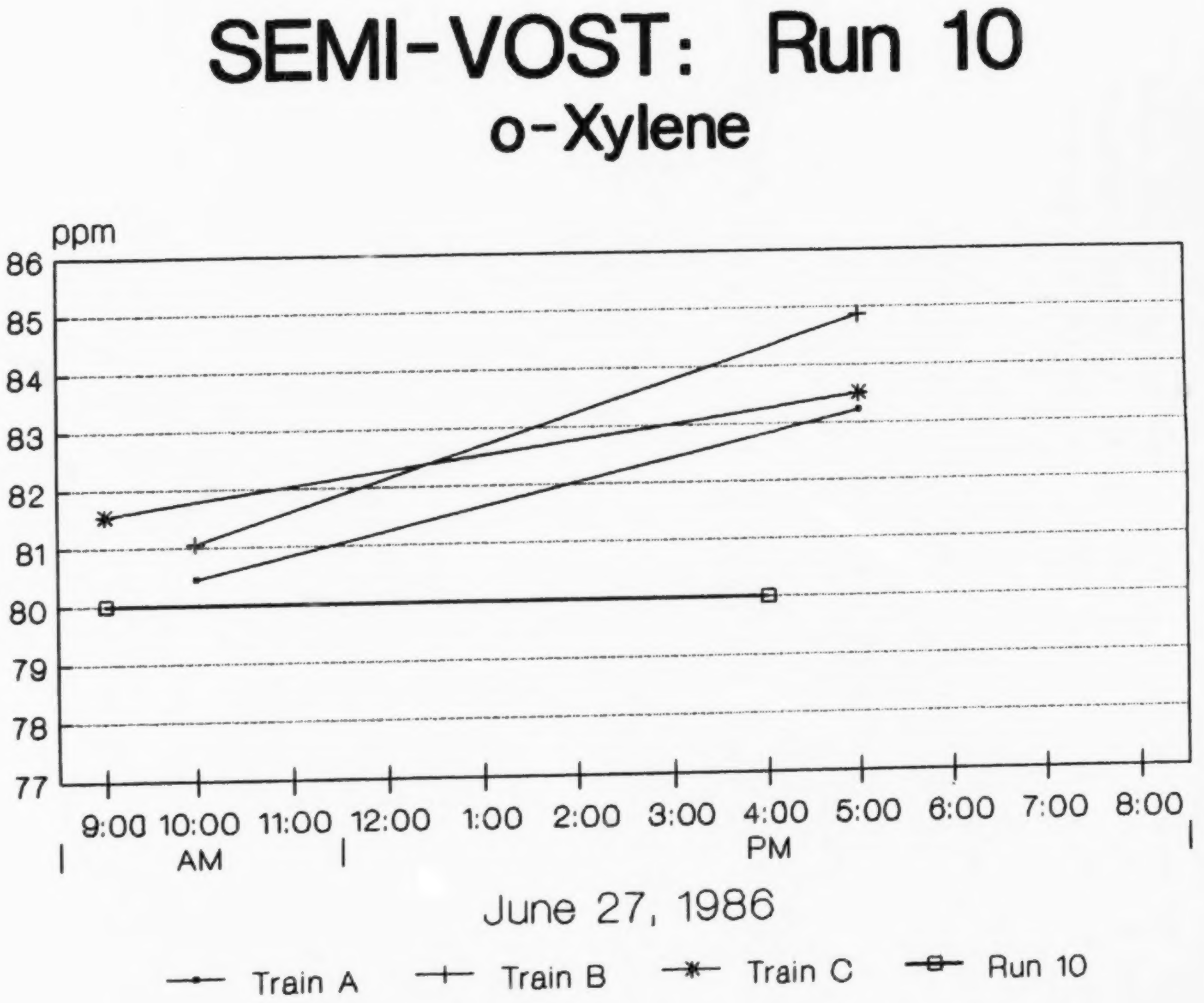


Figure C-55. Concentration vs time.



SEMI-VOST: Run 10

o-Xylene

June 27, 1986

Figure C-56. Concentration vs time.

The concentrations were calculated by direct comparison of the area counts of the sample to the area counts of a quality control cylinder. Each time a sample was taken, an average response factor was calculated using QC data from before and after the sample was injected into the GC and the concentrations of the components reported by Scott Specialty Gases.

APPENDIX C-1.

DYNAMIC SPIKING SYSTEM SOP

RADIAN
CORPORATION

CONFIDENTIAL

RESEARCH & ENGINEERING

STANDARD OPERATING PROCEDURE

GROUP OR LABORATORY: Perimeter Park, RTP	PROCEDURE NO: 318-DS-013		PAGE: 1 of 17
TITLE: OPERATION OF DYNAMIC SPIKING SYSTEM	REVISION NO: Original	EFFECTIVE DATE: October 86	
	SUPERCEDES: NA		
REFERENCES: N/A			
SATELLITE FILES: N/A			
REASON FOR REVISION: N/A			

1.0 PURPOSE

1.1 The purpose of this SOP is to outline the proper operating procedures for the dynamic spiking system.

2.0 DESCRIPTION

2.1 The dynamic spiking system is shown in Figure 1. Specific components of the dynamic spiking system include separate pressure regulators and precision flow controllers for each channel, a heat lamp, circulating fan, and a temperature controller to maintain constant temperature in the control box. A multichannel flow controller readout for monitoring the flow controllers is also included.

Teflon lines connect the flow controllers to the gas supply and to three way valves, used to direct the spike gas into the apparatus to be spiked or to the atmosphere, for flow verification and general venting during equilibration periods.

The components of the spiking system which come in contact with the gases are either stainless steel or teflon.

3.0 SAFETY

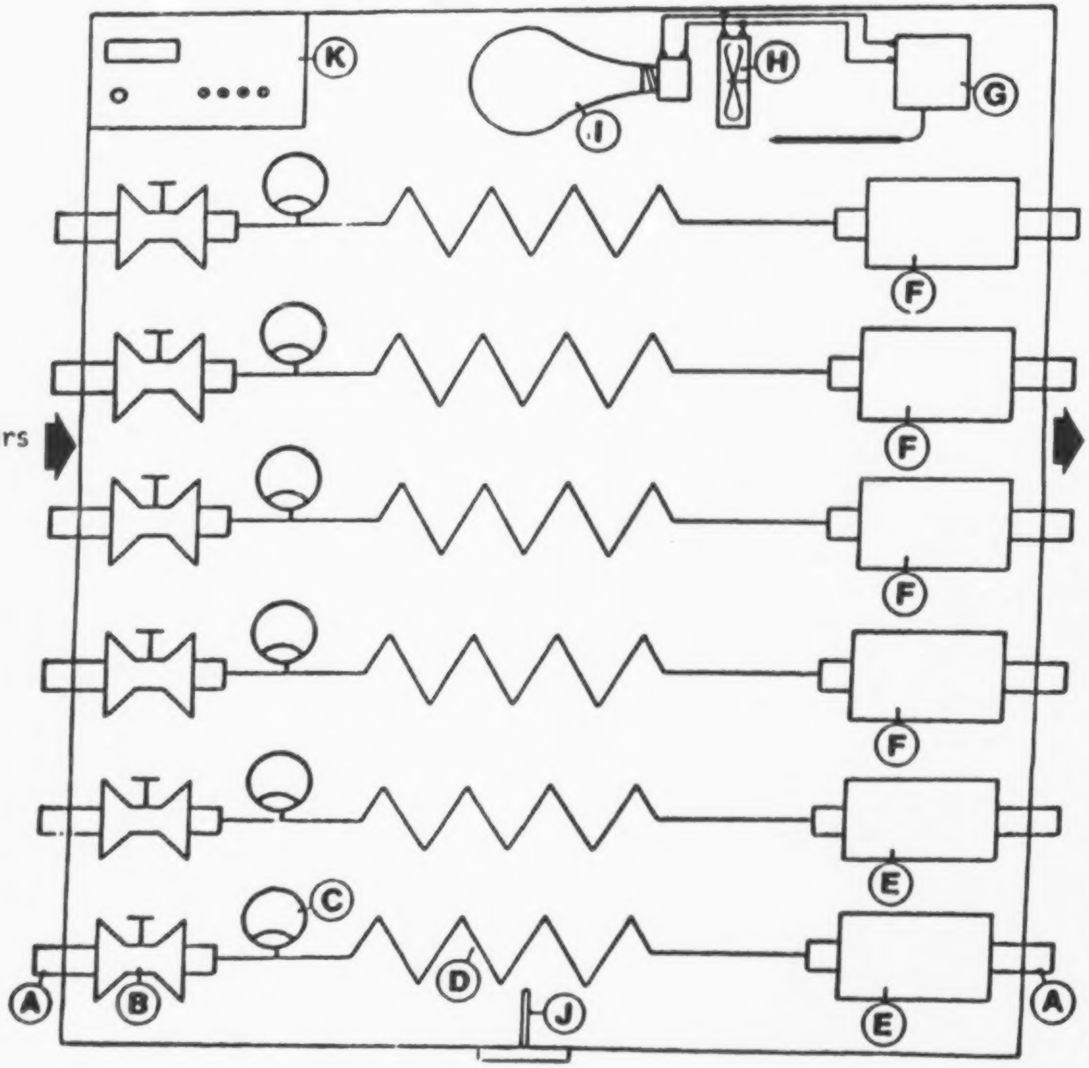
3.1 There are two possible hazards associated with using this system:

1. The gas used may be so corrosive that it damages the system.
2. The gas used may leak out of the system.

3.2 When using this system, take the following precautions:

1. Check to see if the gas to be used is corrosive to stainless steel or teflon.

WRITER: NAME/DATE Joette Steger/10-23-86		
ACTIVITY MGR: NAME/DATE Denny E Wagoner	NAME/DATE Donna J. Holder 10/29/86	NAME/DATE


Gases from cylinders
To Semi-VOST Sample Trains
A
B
C
D
E
E
F
F
F
F
G
H
I
J
K
A

A - 1/4" S.S. Bulk Head Union
B - 0-50 psig Regulator
C - Pressure Gauge
D - 1/4" O.D. x 36" long Preheater CoN
E - Flow Controller's (0-10 elpm) for NO_x Injection
F - Flow Controller's (0-50 asfm) for Mixture of Dioxane Injection
G - 30°-120°F Temp. Controller
H - Circulating Run Fan
I - Heat Lamp
J - Thermometer
K - Flow Controller Common Readout

Figure 1. Spiking System

2. Leak check all connections between the spiking system and all connecting tubing.

4.0 PROCEDURE

4.1 Start-up

1. Plug the dynamic spiking system into a 120 V (ac) power outlet.

2. Turn thermostat on front to 90°F. Thermostat will regulate the system to 90°F ± 5°F.

3. Adjust secondary pressure on the supply cylinder regulator to 40 psi (2.8 kg/cm2).

4. Open shut-off valve(s) on the dynamic spiking system for the channel(s) to be used.

5. Adjust pressure on the flow controller to 20 psi. This should be done slowly to avoid over pressurizing the flow controller. The flow controller requires a minimum pressure drop of 20 psig (1.4 kg/cm^2) for proper operation.

6. Set the flow controller readout to give the desired flow rate. Channels 1 to 4 have been calibrated at these operating conditions and the calibration curves are included here. (Calibration curves should be checked for accuracy on a periodic basis and reestablished if necessary.)

7. Allow the system to equilibrate for at least 2 hours if using 10 ft Teflon lines (1/8" diameter). Longer or different types of line may require longer equilibration times.

8. Verify the flow rates using a bubble flow meter.

3.2 Shut-down

1. Turn supply cylinder(s) off.

2. Allow pressure to bleed out of system.

3. Back flow controller regulator(s) out so that no pressure will register when the system is started back up.

4. Close shut-off valve(s).

5. Turn off thermostat.

6. Turn off flow control readout.

7. Unplug.

5.0 DOCUMENTATION

1. Monitor the flow readouts and pressure regulators periodically.

2. Take flow measurements before and after each test and during any breaks in testing.

3. Complete a data sheet. (An example data sheet is included in Figure 2.)

6.0 QUALITY CONTROL

1. Always check the flow rate using a bubble flow meter before starting a test.

2. If the measured flow rate is not within 10 percent of the expected flow rate as determined by the latest calibration, recalibrate the system.

3. If for some reason, any other conditions (i.e. temperature or pressure) need to be used; calibrate the system using these conditions.

4. When the system is recalibrated, replace the calibration data in this SOP with the new calibration data. Include the following information:

   a) person who did the calibration,
   b) thermostat setting,
   c) pressure regulator settings,
   d) room temperature,
   e) barometric pressure, and
   f) date calibration performed.

7.0 REVIEW AND VALIDATION

The task leader in charge of the project using the spiking system is responsible to see that the system is calibrated properly and used safely and correctly.

OPERATIONAL [illegible] DYNAMIC [illegible] FLOW RATES (ML/MIN)

			SET FLOW				FLOW DIAL READING				MEASURED FLOW ON [illegible] FLOW METER			
TEST ID	DATE	TIME	CHAN. 1	CHAN. 2	CHAN. 3	CHAN. 4	CHAN. 1	CHAN. 2	CHAN. 3	CHAN. 4	CHAN. 1	CHAN. 2	CHAN. 3	CHAN. 4

Figure 2. Data Sheet

```
                                                    SUMMARY STATISTICS - LINEAR REG
                                                    CHANNEL 1, 0-50 cc/MIN.

  Your        Your       Regr        2.5th       97.5th
x - data    y - data     Line        C.I.         C.I.

   5.00        3.66    2.960495   -2.07257    7.993564
  10.00        8.61    8.429329   4.441421    12.41723          10 = n
  15.00       13.87    13.89816   10.92706    16.86926       275.4 = Sum of x
  20.00       19.17    19.36699   17.34120    21.39279      276.14 = Sum of y
  25.10       24.31    24.94520   23.63784    26.25257     9651.04 = Sum of x^2
  30.10       30.24    30.41404   29.09592    31.73215    10100.21 = Sum of y^2
  35.10       35.09    35.88287   33.85358    37.91217    9865.191 = Sum of x*y
  40.10       41.27    41.35171   38.37664    44.32678       27.54 = x mean
  45.00       46.73    46.71116   42.73981    50.68252      27.614 = y mean
  50.00       53.19    52.18000   47.16378    57.19621    2066.524 = Sum of x^2-(Sum of
                                                          2474.887 = Sum of y^2-(sum of
                                                          2260.295 = Sum of x*y-(sum of

                                                          1.093766 = Slope (m)
                                                          -2.50833 = Intercept (b)
                                                          0.999464 = Coefficient of Cor

                                                          0.575663 = Sd of points about t
```

```
                                              SUMMARY STATISTICS - LINEAR REG
                                              CHANNEL 2, 0-100 cc/MIN.
 ----------------------------------------------------------------------------

 ----------------------------------------------------------------------------
   Your       Your      Regr       2.5th      97.5th
 x - data   y - data    Line       C.I.        C.I.

    5.10       5.91   6.055254   3.581923   8.528585          10 = n
   10.00      11.42   11.60153   9.629708   13.57336       275.1 = Sum of x
   15.00      17.24   17.26100   15.78537   18.73663      314.21 = Sum of y
   20.00      23.16   22.92047   21.90230   23.93864     9625.03 = Sum of x^2
   25.10      28.60   28.69313   28.01483   29.37143    12508.95 = Sum of y^2
   29.90      34.45   34.12622   33.44873   34.80372    10972.25 = Sum of x*y
   35.00      39.89   39.89888   38.88239   40.91537       27.51 = x mean
   40.00      45.72   45.55835   44.08466   47.03205      31.421 = y mean
   45.00      51.55   51.21782   49.24802   53.18762    2057.029 = Sum of x^2-(Sum of
   50.00      56.27   56.87729   54.39570   59.35889    2636.163 = Sum of y^2-(sum of
                                                       2328.338 = Sum of x*y-(sum of

                                                       1.131894 = Slope (m)
                                                       0.282594 = Intercept (b)
                                                       0.999861 = Coefficient of Cor

                                                       0.302226 = Sd of points about t
 ----------------------------------------------------------------------------
```

```
                                SUMMARY STATISTICS - LINEAR REG
                                CHANNEL 3, 50 cc/MIN.
___________________________________________________________________________
___________________________________________________________________________
   Your      Your       Regr        2.5th       97.5th
 x - data  y - data     Line        C.I.         C.I.

    5.00      5.95    5.712181    4.251244    7.173119          10 = n
   10.00     11.41    11.42103    10.26128    12.58077         275 = Sum of x
   15.00     17.11    17.12987    16.26212    17.99763      314.02 = Sum of y
   20.00     22.71    22.83872    22.24012    23.43733        9625 = Sum of x^2
   25.00     28.41    28.54757    28.14633    28.94881    12549.86 = Sum of y^2
   30.00     33.98    34.25642    33.85518    34.65766    10990.45 = Sum of x*y
   35.00     40.11    39.96527    39.36666    40.56387        27.5 = x mean
   40.00     45.66    45.67412    44.80636    46.54187      31.402 = y mean
   45.00     51.63    51.38296    50.22322    52.54271      2062.5 = Sum of x^2-(Sum of
   50.00     57.05    57.09181    55.63088    58.55275    2689.006 = Sum of y^2-(sum of
                                                            2354.9 = Sum of x*y-(sum of

                                                          1.141769 = Slope (m)
                                                          0.003333 = Intercept (b)
                                                          0.999952 = Coefficient of Cor

                                                          0.177799 = Sd of points about t
___________________________________________________________________________
```

```
                                   SUMMARY STATISTICS - LINEAR REG
                                   CHANNEL 4, 100 cc/MIN.

  Your        Your      Regr        2.5th       97.5th
x - data    y - data    Line        C.I.         C.I.

   5.00        9.90   9.661272   6.112622   13.20992
  10.00       15.42   15.37854   12.55486   18.20222         10 = n
  15.00       21.08   21.09581   18.97252   23.21910        275 = Sum of x
  20.00       26.36   26.81309   25.33036   28.29582     353.89 = Sum of y
  25.00       32.33   32.53036   31.50881   33.55190       9625 = Sum of x^2
  30.00       38.96   38.24763   37.22609   39.26918   15222.17 = Sum of y^2
  35.00       43.35   43.96490   42.48217   45.44763   12090.35 = Sum of x*y
  40.00       50.08   49.68218   47.55889   51.80547       27.5 = x mean
  45.00       54.95   55.39945   52.57577   58.22313     35.389 = y mean
  50.00       61.46   61.11672   57.56807   64.66537     2062.5 = Sum of x^2-(Sum of
                                                     2698.362 = Sum of y^2-(Sum of
                                                     2358.375 = Sum of x*y-(Sum of

                                                     1.143454 = Slope (m)
                                                        3.944 = Intercept(b)
                                                     0.999690 = Coefficient of Cor

                                                     0.456628 = Sd of points about t
```

CHANNEL # 1
Reg. @ 20 psig. = Sec. Tank psig = 60
Temp. @ 90°F (F.C.'s)
Temp @ 72°F (Room)
Pb = 753.0 Checkout Gas = N_2

INDICATED FLOW	MEASURED FLOW	0 FLOW = 0 FLOW
5.0	1.0 cc/.272, .274, .274 = .2733	= 3.66 cc/min.
10.0	10.0 cc/1.161, 1.162, 1.161 = 1.1613	= 8.61 cc/min.
15.0	10.0 cc/.723, .719, .721 = .7210	= 13.87 cc/min.
20.0	10.0 cc/.521, .522, .522 = .5217	= 19.17 cc/min.
25.1	10.0 cc/.409, .413, .412 = .4113	= 24.31 cc/min.
30.1	10.0 cc/.327, .334, .331 = .3307	= 30.24 cc/min.
35.1	10.0 cc/.283, .286, .286 = .2850	= 35.09 cc/min.
40.1	10.0 cc/.246, .241, .240 = .2423	= 41.27 cc/min.
45.0	10.0 cc/.212, .216, .214 = .2140	= 46.73 cc/min.
50.0	10.0 cc/.185, .190, .189 = .1880	= 53.19 cc/min.

CHANNEL # 2
Reg. @ 20 psig. = Sec. Tank psig = 60
Temp. @ 90°F (F.C.'s)
Temp @ 72°F (Room)
Pb = 753.0

Checkout Gas = N_2

INDICATED FLOW	MEASURED FLOW	0 FLOW = 0 FLOW
5.1	1.0 cc/.168, .170, .170 = .1693	= 5.91 cc/min.
10.0	10.0 cc/.874, .879, .875 = .8760	= 11.42 cc/min.
15.0	10.0 cc/.584, .577, .579 = .5800	= 17.24 cc/min.
20.0	10.0 cc/.430, .433, .432 = .4317	= 23.16 cc/min.
25.10	10.0 cc/.350, .349, .350 = .3497	= 28.60 cc/min.
29.9	10.0 cc/.294, .286, .291 = .2903	= 34.45 cc/min.
35.0	10.0 cc/.251, .251, .250 = .2507	= 39.89 cc/min.
40.0	10.0 cc/.214, .221, .221 = .2187	= 45.72 cc/min.
45.0	10.0 cc/.193, .195, .194 = .1940	= 51.55 cc/min.
50.0	10.0 cc/.177, .178, .178 = .1777	= 56.27 cc/min.

CHANNEL # 3
Reg. @ 20 psig. = Sec. Tank psig = 60
Temp. @ 90°F (F.C.'s)
Temp @ 72°F (Room)
Pb = 753.0

Checkout Gas = N_2

INDICATED FLOW	MEASURED FLOW	0 FLOW = 0 FLOW
5.0	1.0 cc/.167, .169, .168 = .1680	= 5.95 cc/min.
10.0	10.0 cc/.877, .875, .876 = .8760	= 11.41 cc/min.
15.0	10.0 cc/.591, .574, .588 = .5843	= 17.11 cc/min.
20.0	10.0 cc/.438, .443, .440 = .4403	= 22.71 cc/min.
25.0	10.0 cc/.356, .349, .351 = .3520	= 28.41 cc/min.
30.0	10.0 cc/.293, .296, .294 = .2943	= 33.98 cc/min.
35.0	10.0 cc/.251, .248, .249 = .2493	= 40.11 cc/min.
40.0	10.0 cc/.221, .217, .219 = .2190	= 45.66 cc/min.
45.0	10.0 cc/.194, .193, .194 = .1937	= 51.63 cc/min.
50.0	10.0 cc/.174, .176, .176 = .1753	= 57.05 cc/min.

CHANNEL # 4

Reg. @ 20 psig. = Sec. Tank psig = 60

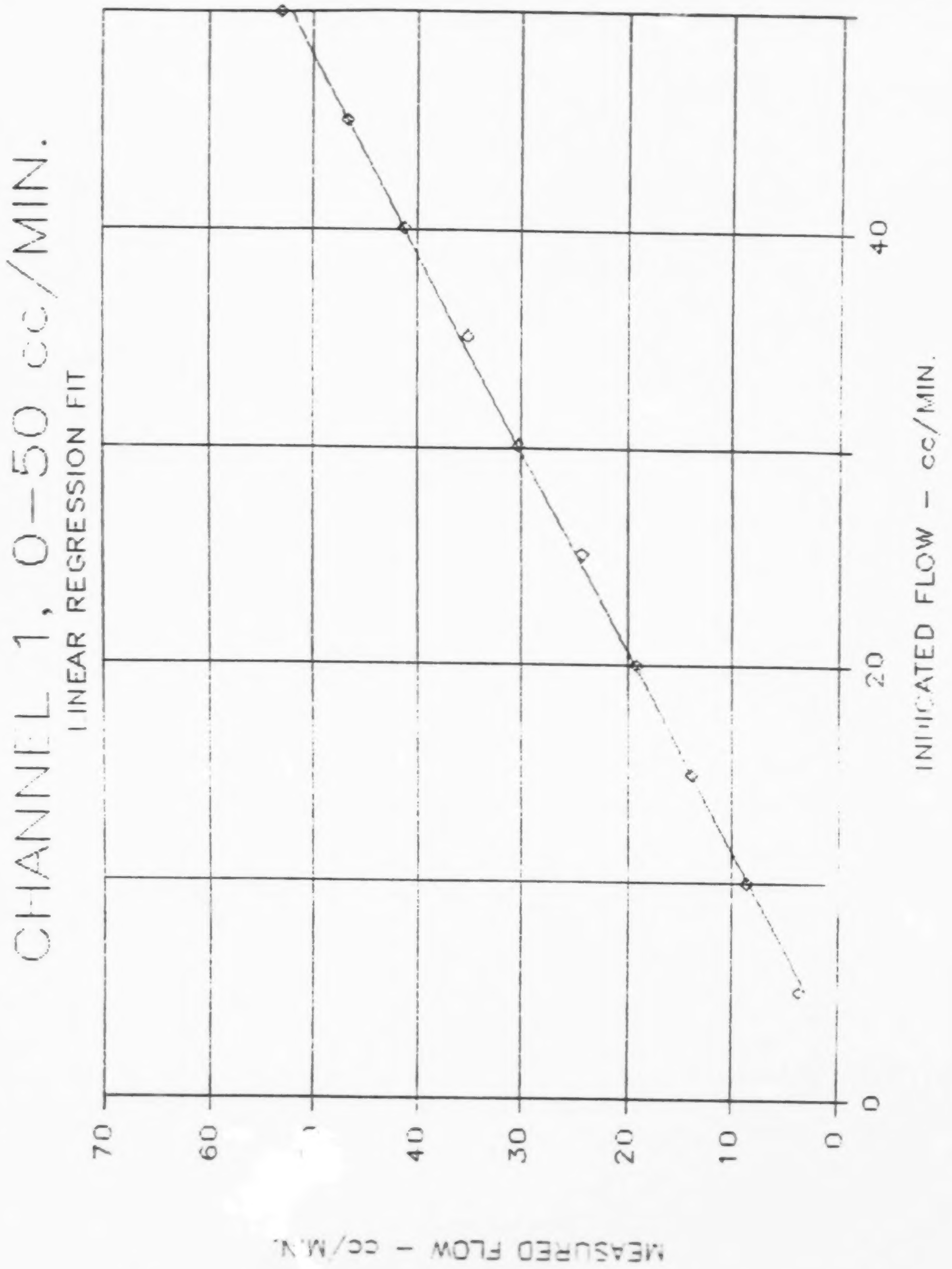
Temp. @ 90°F (F.C.'s)

Temp @ 72°F (Room)

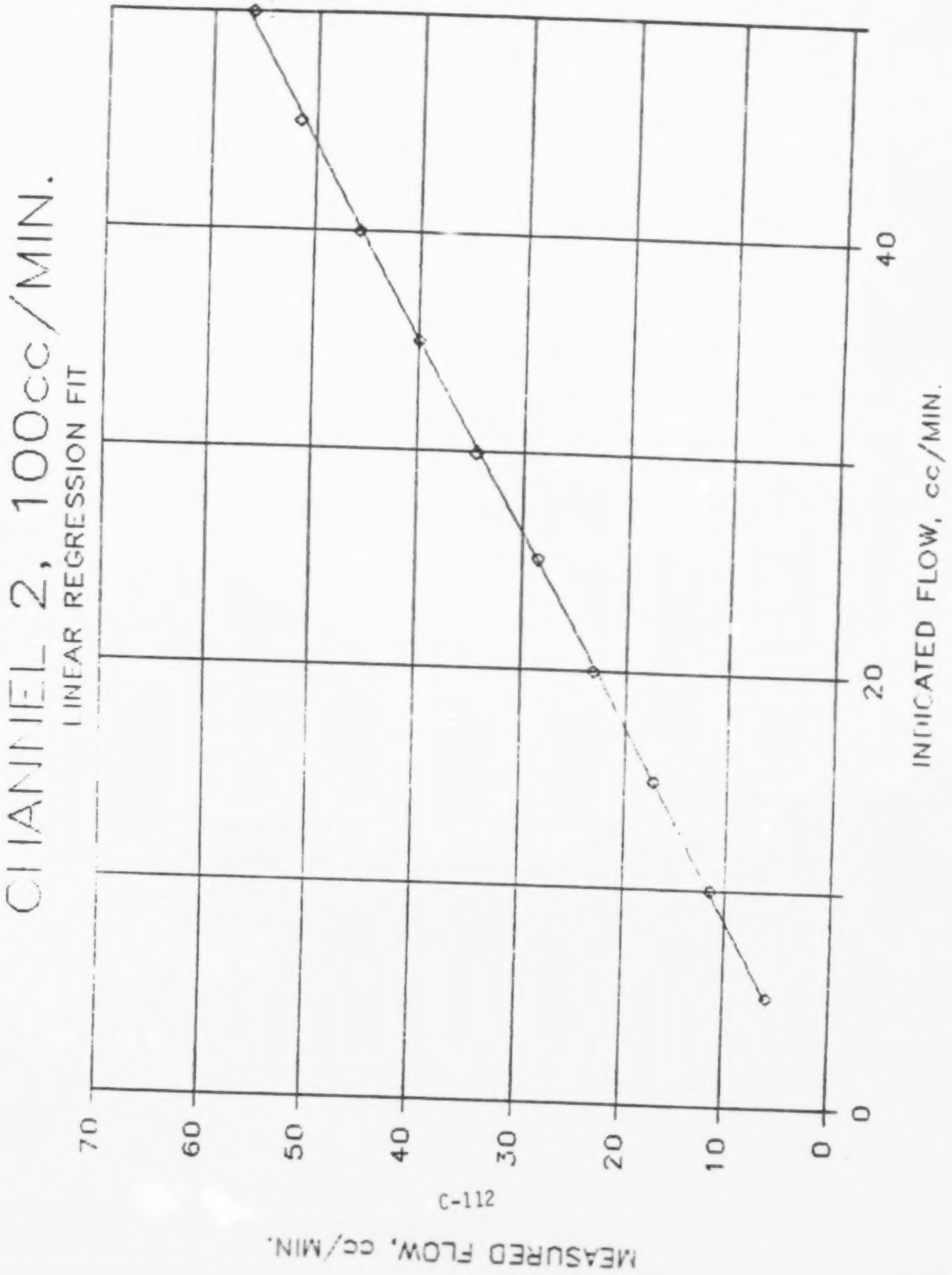
Pb = 753.0

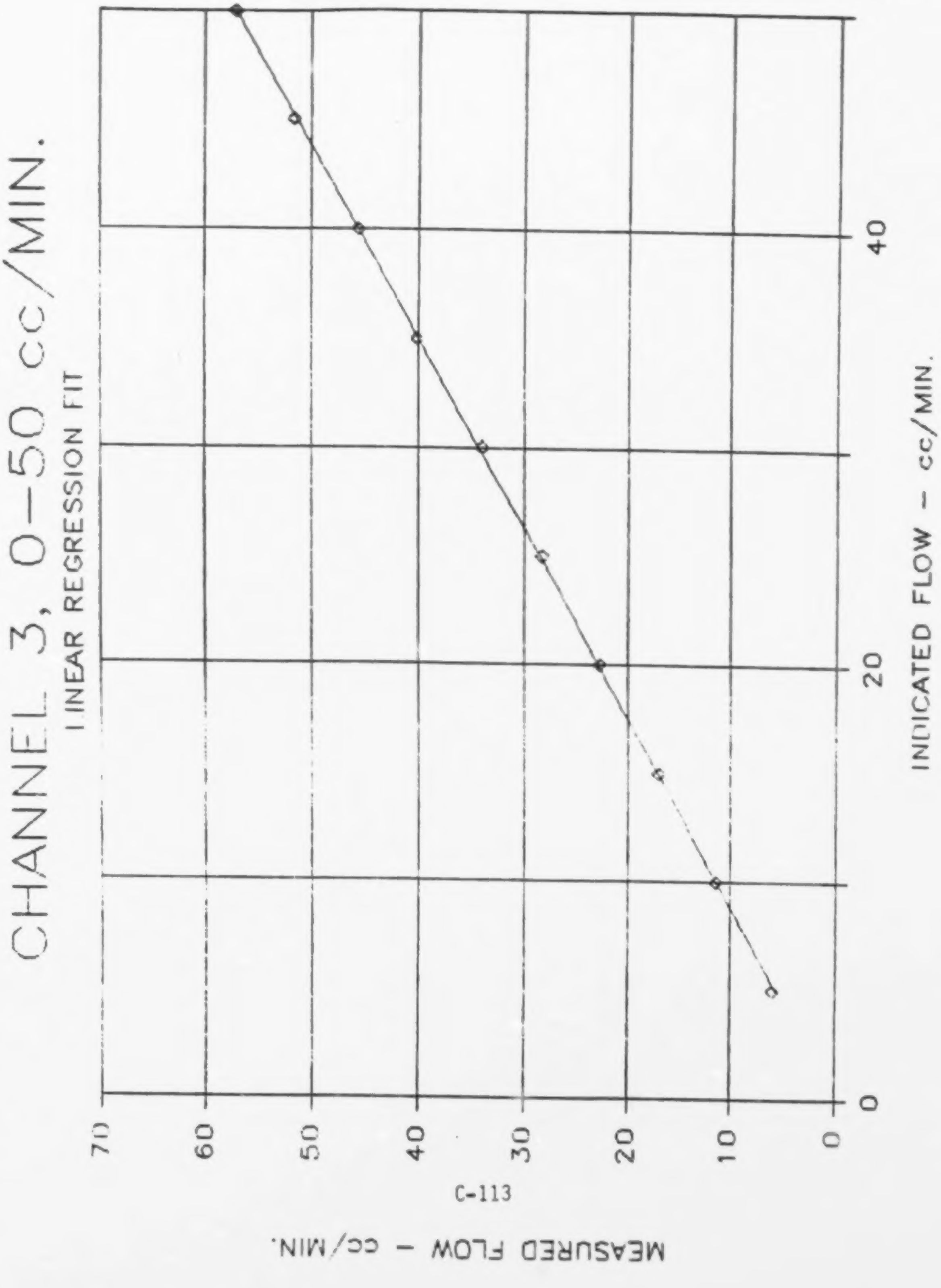
Checkout Gas = N_2

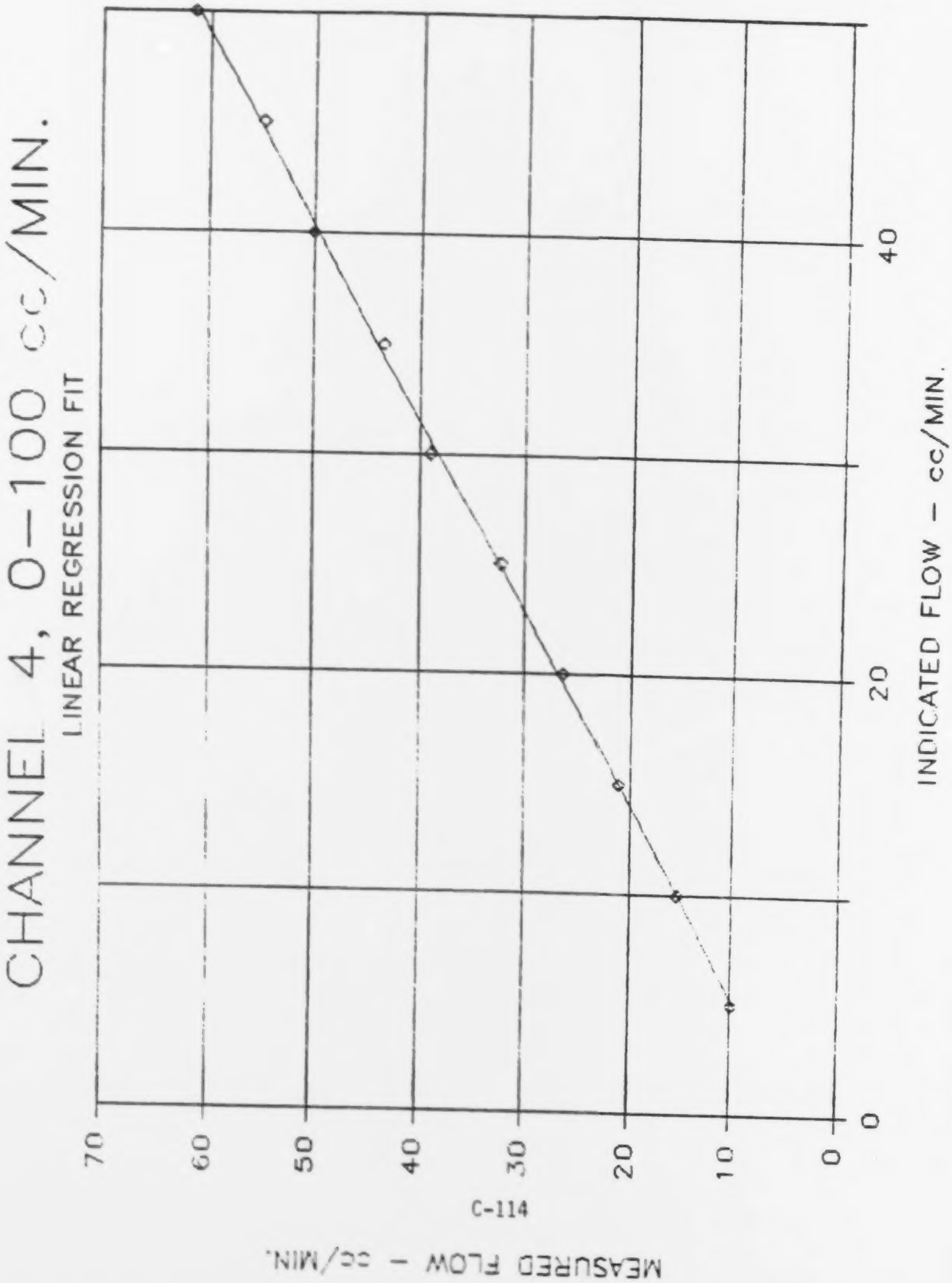
INDICATED FLOW	MEASURED FLOW	0 FLOW = 0 FLOW
5.0	1.0 cc/.101, .101, .101 = .1010	= 9.90 cc/min.
10.0	10.0 cc/.648, .648, .649 = .6483	= 15.42 cc/min.
15.0	10.0 cc/.473, .476, .474 = .4743	= 21.08 cc/min.
20.0	10.0 cc/.378, .380, .380 = .3793	= 26.36 cc/min.
25.0	10.0 cc/.311, .308, .309 = .3093	= 32.33 cc/min.
30.0	10.0 cc/.258, .252, .260 = .2567	= 38.96 cc/min.
35.0	10.0 cc/.231, .230, .231 = .2304	= 43.35 cc/min.
40.0	10.0 cc/.199, .200, .200 = .1997	= 50.08 cc/min.
45.0	10.0 cc/.181, .183, .182 = .1820	= 54.95 cc/min.
50.0	10.0 cc/.164, .162, .162 = .1627	= 61.46 cc/min.


CHANNEL 1, 0-50 cc/MIN.
LINEAR REGRESSION FIT
0
20
40
INDICATED FLOW - cc/MIN.
70
60
40
30
20
10
0
MEASURED FLOW - cc/MIN.

PROCEDURE NO:	PAGE:
318-DS-013	16 of 17




CHANNEL 3, 0–50 cc/MIN.
LINEAR REGRESSION FIT
INDICATED FLOW – cc/MIN.
0
20
40
MEASURED FLOW – cc/MIN.
70
60
50
40
30
20
10
0



CHANNEL 4, 0–100 cc/MIN.

LINEAR REGRESSION FIT

APPENDIX D

ANALYTICAL PROCEDURES AND RESULTS

Samples were analyzed by capillary GC/MS/DS, using the method of response factors. The instrument was tuned daily to meet EPA criteria for decafluorotriphenylphosphine (DFTPP). No analyses were performed until the system met DFTPP tuning criteria. The values obtained for the daily DFTPP analysis are shown in Appendix E, Table E-5. When analysis was initiated, system calibration was the first operation completed.

A series of calibration standards was prepared from the compounds of interest, surrogates, and quantitation standards so that the range of the compounds of interest spanned the linear working range of the instrumentation. Each of these standards was then analyzed, in duplicate, using the same conditions, to develop a response-concentration data pair. The response factors which span the concentration range were placed into a database, and the means of these response factor values were determined and used to perform quantitative calculations. Three response factor databases were generated in the course of this study. Whenever analysis of the daily calibration standard showed that sufficient instrument drift had occurred (±20%), a new database was developed. Mean values of the response factors for each database with the standard deviation and coefficient of variation are shown in Table D-1.

In the daily analytical protocol, the first analysis of each day was decafluorotriphenylphosphine (DFTPP), which was used to demonstrate that tuning criteria were being met. The second sample analyzed each day was a calibration sample. The purpose of the daily analysis of the calibration sample was to establish the validity of the current database. Daily calibration samples are tabulated and control charts for these calibration samples relative to the appropriate database are

TABLE D-1. RESPONSE FACTOR DATABASES

		Database #1			Database #2			Database #3		
Compound	M/Z	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
[1]d_5-pyridine	84	1.379	0.209	15	1.303	0.357	27	1.435	0.193	13
[1]pyridine	79	1.371	0.181	13	1.212	0.320	26	1.426	0.198	14
[1]d_8-toluene	98	2.446	0.189	8	2.316	0.381	16	2.443	0.156	6
[1]toluene	92	1.658	0.172	10	1.521	0.309	20	1.783	0.126	7
[1]tetrachloroethene	164	0.389	0.015	4	0.508	0.057	11	0.353	0.030	9
[1]d_5-chlorobenzene	177	1.632	0.116	7	1.572	0.296	19	1.581	0.139	9
[1]chlorobenzene	112	1.648	0.133	8	1.511	0.278	20	1.625	0.143	9
[1]d_{10}-ethylbenzene	116	0.937	0.036	4	1.036	0.046	4	0.842	0.019	2
[1]d_{10}-o-xylene	116	0.955	0.073	8	0.995	0.191	19	0.948	0.080	8
[1]o-xylene	100	0.998	0.099	10	0.903	0.211	23	1.000	0.095	10
[2]d_2-tetrachloroethane	84	1.056	0.081	8	1.140	0.269	24	0.965	0.132	14
[2]tetrachloroethane	83	1.039	0.095	9	1.116	0.266	24	0.965	0.132	14
[2]d_5-phenol	99	1.016	0.075	7	1.317	0.096	7	0.893	0.060	7
[2]d_5-nitrobenzene	82	0.717	0.083	12	0.664	0.091	14	0.683	0.101	15
[2]d_5-nitrobenzene	128	0.224	0.023	10	0.294	0.033	11	0.213	0.021	10
[2]d_8-naphthalene	136	1.369	0.154	11	1.616	0.132	8	1.209	0.106	9

[1] Response factor calculated relative to d_{10}-p-xylene.

[2] Response factor calculated relative to d_5-bromobenzene.

shown in Appendix E. The final analysis of every day was the analysis of a control sample. Results for the daily analysis of this control sample are shown in Appendix E.

The average relative response factor for a given compound was calculated in the following way:

1) An area count for the ion selected for quantitation was obtained from duplicate injections of each of the five levels of calibration standards. Each standard contained a known amount of the test compounds with a known amount of the surrogates and quantitation standards. The area used for each compound was an ion peak area, usually the major ion. For the quantitative calculations, the major ion of d_{10}-o-xylene was 116, that of d_5-bromobenzene was 82, and that of d_{10}-phenanthrene was 188.
2) A relative response factor was calculated in duplicate for each compound at each concentration level using the equation below:

$$RRF = \frac{A_s C_{is}}{A_{is} C_s}$$

where

A_s = area of the characteristic ion for the compound to be measured

A_{is} = area of the characteristic ion for the quantitation standard

C_{is} = concentration of internal standard (ug/mL)

C_s = concentration of the compound to be measured

Relative response factors were averaged for each compound at each level over the entire concentration range.

The concentration of any given POHC in the gaseous emission of a combustion process is then calculated using the following equation:

$$C_{POHC} = \frac{C_{is}}{A_{is}} \times \frac{A_{POHC}}{RRF}$$

where

A_{POHC} = area of the major ion for the POHC of interest

A_{is} = area of the major ion for the quantitation standard

C_{is} = concentration of the quantitation standard spiked into the sample (ug/mL)

C_{POHC} = concentration of the compound of interest (ug/mL)

RRF = average relative response factor for the POHC of interest

The three response factor databases generated for the analysis of the field samples are presented in Table D-1. To obtain the total amount of compound collected, the concentration of the POHC is multiplied by the final extract volume, ultimately dividing the final answer by the volume of stack gas sampled. Percent recovery for the surrogate compounds was determined by dividing the amount of any single surrogate spiked into a sample before sample preparation into the amount of that surrogate found to be in the sample after analysis and multiplying by 100. Results obtained for all the train components analyzed are shown in Table D-2. Data are grouped by Run. Surrogate recoveries for all of the Runs are summarized in Table 6-6.

The values reported in Table D-2 are not corrected for surrogate recoveries. Surrogate recoveries can be used to assess the efficiency of the method for recovering compounds from the matrix. Corrections can validly be made to allow for less than 100 percent recovery of surrogate compounds and the corrected values will then reflect recoveries of surrogates. Measured amounts of test compounds can be adjusted by using the ratio of the surrogate recovery of d_{10}-ethylbenzene spiked in the samples to the recovery of this compound from the Research Triangle control samples. A series of control samples prepared by the Research Triangle Institute was analyzed to support Radian analytical data for the Semi-VOST field samples. The Research Triangle Institute prepared control samples which were spiked onto XAD-2® resin. The mean recovery values of the deuterated compounds used during the analysis of the

TABLE D-2. VALIDATED GC/MS DATA

Compound	5AACS23 FB-01[3]	5AACS24 FB-02[3]	5AAC374 01A SM, F	5AAC373 01C SM, F	5AAC375 01D SM, F	5AAC362 03A PR,BH,CD,IR	5AAC360 03B PR,BH,CD,IR	5AAC363 03C PR,BH,CD,IR	5AAC364 03D PR,BH,CD,IR
d_5-pyridine	ND[2]	ND	2837	3268	2875	3151	1194	3281	3367
pyridine	ND	ND	ND	ND	ND	ND	ND	ND	ND
d_8-toluene	ND	ND	177	330	299	514	108	533	475
toluene	ND	ND	9	6	8	23	19	21	11
tetrachloroethene	ND	ND	ND	ND	ND	ND	ND	ND	ND
d_5-chlorobenzene	ND	ND	56	72	57	80	20	94	85
chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND
d_{10}-ethylbenzene[1]	15(2)	6(1)	556(58)	563(59)	747(78)	681(71)	147(77)	697(73)	718(75)
d_{10}-*o*-xylene	ND	ND	583	705	444	748	139	761	669
o-xylene	ND	ND	3	ND	3	ND	6	3	4
d_2-tetrachloroethane	ND	ND	35	35	24	36	8	43	44
tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND
d_5-phenol	1446(63)	1561(67)	2054(88)	1970(84)	1975(84)	1529(65)	2254(96)	1945(83)	2389(102)
d_5-nitrobenzene	400(72)	448(82)	417(76)	346(63)	464(87)	306(56)	64(58)	324(59)	368(67)
d_8-naphthalene	88(53)	104(63)	107(65)	90(54)	118(71)	92(56)	31(19)	95(58)	100(61)

[1] Value in parentheses is Surrogate Recovery (%).

[2] Not Detected.

[3] Field blanks.

TABLE D-2. Continued

Compound	5AAC365 04A PR,BH,CD,IR	5AAC361 04B PR,BH,CD,IR	5AAC366 04C PR,BH,CD,IR	5AAC376 04D PR,BH,CD,IR	5AAC388 05A PR,BH,CD,IR	5AAC389 05B PR,BH,CD,IR	5AAC407 05C PR,BH,CD,IR	5AAC408 05D PR,BH,CD,IR
d_5-pyridine	2378	2284	2481	2724	3427	1953	2848	3520
pyridine	ND	ND	ND	ND	ND	ND	ND	ND
d_8-toluene	438	392	481	427	429	477	545	631
toluene	90	50	67	182	56	55	23	38
tetrachloroethene	ND	ND	ND	ND	ND	ND	ND	ND
d_5-chlorobenzene	68	65	87	101	65	73	69	94
chlorobenzene	ND	3	3	42	85	ND	ND	ND
d_{10}-ethylbenzene	584(61)	568(60)	593(62)	563(59)	644(67)	590(62)	586(61)	587(61)
d_{10}-o-xylene	606	591	699	712	650	703	671	696
o-xylene	2	2	3	35	14	7	ND	ND
d_2-tetrachloroethane	32	31	41	57	26	26	40	38
tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND
d_5-phenol	1550(66)	1916(82)	1931(83)	64(3)	1120(48)	1856(79)	1352(58)	1474(63)
d_5-nitrobenzene	278(50)	277(50)	296(54)	579(105)	327(60)	279(51)	323(59)	324(59)
d_8-naphthalene	80(49)	86(53)	84(51)	138(84)	90(55)	78(47)	71(43)	70(43)

TABLE D-2. Continued

Compound	5AAC507 06A FRONT	5AAC508 06A BACK	5AAC509 06B FRONT	5AAC499 06B BACK	5AAC510 06C FRONT	5AAC498 06C BACK	5AAC500 06D FRONT	5AAC511 06D BACK
d_5-pyridine	343	4263	182	4128	384	3734	ND	ND
pyridine	ND	ND	ND	ND	ND	ND	ND	ND
d_8-toluene	142	ND	58	3	978	ND	3	1
toluene	35	14	6	13	31	17	40	15
tetrachloroethene	ND	ND	ND	13	5	ND	12	10
d_5-chlorobenzene	55	ND	25	ND	219	ND	ND	ND
chlorobenzene	ND	ND	ND	9	14	16	23	13
d_{10}-ethylbenzene	206(20)	47(49)	91(9)	55(58)	851(81)	61(6)	856(81)	26(28)
d_{10}-o-xylene	348	ND	146	4	1237	ND	4	3
o-xylene	ND	ND	ND	5	7	9	8	5
d_2-tetrachloroethane	70	ND	26	ND	ND	ND	ND	ND
tetrachloroethane	ND	ND	ND	ND	0.6	ND	ND	ND
d_5-phenol	154(66)	165(71)	124(54)	181(77)	165(70)	174(75)	178(76)	169(72)
d_5-nitrobenzene	626(103)	72(130)	500(82)	58(105)	709(117)	58(104)	711(118)	57(103)
d_8-naphthalene	165(91)	18(111)	124(57)	18(118)	193(107)	18(112)	207(115)	13(84)

TABLE D-2. Continued

Compound	5AAC417 07A FRONT	5AACS34 07A FRONT 1/4	AVERAGE 07A	5AACS01 07A BACK 1/4
d_5-pyridine	712	983	848	10691
pyridine	ND	ND	ND	ND
d_8-toluene	1458	1398	1428	6
toluene	93	120	107	24
tetrachloroethene	ND	8	4	ND
d_5-chlorobenzene	330	491	411	ND
chlorobenzene	ND	ND	ND	28
d_{10}-ethylbenzene	615(64)	843(88)	729(76)	ND
d_{10}-o-xylene	6023	3831	4927	ND
o-xylene	ND	3	2	22
d_2-tetrachloroethane	182	423	303	ND
tetrachloroethane	ND	ND	ND	ND
d_5-phenol	1488(64)	2286(98)	1887(81)	3370(141)
d_5-nitrobenzene	264(48)	660(120)	462(84)	ND
d_8-naphthalene	84(51)	205(124)	145(104)	ND

TABLE D-2. Continued

Compound	5AAC427 07B FRONT	5AAC502 07B BACK	5AAC428 07C FRONT	5AAC505 07C BACK	5AAC429 07D FRONT	5AAC504 07D BACK
d_5-pyridine	794	12124	1101	10526	ND	ND
pyridine	ND	ND	ND	ND	ND	ND
d_8-toluene	1633	3	1334	4	ND	ND
toluene	142	9	124	9	171	7
tetrachloroethene	ND	14	ND	16	ND	25
d_5-chlorobenzene	372	2	355	ND	ND	ND
chlorobenzene	ND	10	14	12	9	13
d_{10}-ethylbenzene	548(57)	370(70)	670(70)	340(36)	63(66)	250(26)
d_{10}-o-xylene	4562	7	3850	ND	ND	ND
o-xylene	ND	6	8	8	6	10
d_2-tetrachloroethane	211	5	243	ND	ND	ND
tetrachloroethane	ND	ND	ND	ND	ND	ND
d_5-phenol	1324(57)	1567(67)	1500(44)	1441(62)	1326(57)	1496(64)
d_5-nitrobenzene	280(51)	591(108)	390(71)	584(106)	323(59)	592(107)
d_8-naphthalene	80(49)	153(92)	100(61)	157(95)	88(53)	152(92)

TABLE D-2. Continued

Compound	5AAC410 08A	5AAC411 08B	5AAC412 08C	5AAC413 08D	5AAC517 09A	5AAC518 09B	5AAC495 09C	5AAC497 09D
d_5-pyridine	2318	2943	5038	5065	3587	4215	4560	4135
pyridine	ND	ND	ND	ND	ND	ND	ND	ND
d_8-toluene	594	598	684	714	752	868	749	754
toluene	55	40	35	32	125	54	32	25
tetrachloroethene	ND	ND	ND	ND	6	11	ND	ND
d_5-chlorobenzene	99	97	90	108	163	176	135	143
chlorobenzene	50	8	15	ND	55	21	19	11
d_{10}-ethylbenzene	649(68)	640(67)	605(63)	618(65)	747(78)	811(85)	818(86)	787(82)
d_{10}-*o*-xylene	740	719	768	806	972	1037	900	681
o-xylene	29	12	13	11	19	13	18	15
d_2-tetrachloroethane	48	46	4[illegible]	45	95	99	60	84
tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND
d_5-phenol	1850(79)	1849(79)	1751(75)	1751(75)	1601(68)	1448(62)	2975(127)	1595(68)
d_5-nitrobenzene	355(64)	351(64)	370(67)	382(70)	628(115)	677(123)	552(100)	636(115)
d_8-naphthalene	84(51)	81(49)	82(49)	81(49)	175(106)	181(109)	179(108)	186(113)

TABLE D-2. Continued

Compound	5AACS31 10A FRONT	5AACS32 10A BACK	5AACS33 10B FRONT	5AACS26 10B BACK	5AACS25 10C FRONT	5AACS29 10C BACK	5AACS27 10D FRONT	5AACS30 10D BACK
d_5-pyridine	882	7302	978	4675	1080	5557	ND	ND
pyridine	ND	ND	ND	ND	ND	ND	ND	ND
d_8-toluene	1719	ND	1175	7	1414	4	ND	ND
toluene	75	10	39	24	70	9	92	8
tetrachloroethene	15	23	11	22	11	20	ND	13
d_5-chlorobenzene	423	ND	342	ND	375	2	ND	ND
chlorobenzene	24	7	10	15	8	7	16	3
d_{10}-ethylbenzene	839(80)	51(53)	779(81)	78(81)	766(73)	55(58)	777(74)	58(61)
d_{10}-*p*-xylene	2567	6	2193	8	2377	5	10	3
p-xylene	13	8	6	9	8	7	13	5
d_2-tetrachloroethane	291	ND	268	ND	246	ND	ND	ND
tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND
d_5-phenol	139(59)	134(57)	159(68)	145(62)	99(42)	128(54)	123(53)	121(52)
d_5-nitrobenzene	650(108)	54(99)	648(107)	53(96)	604(99)	50(91)	629(104)	47(87)
d_8-naphthalene	206(114)	19(124)	202(112)	21(126)	195(107)	19(125)	204(113)	17(115)

TABLE D-3. COMPOUNDS RECOVERED FROM FIELD DYNAMIC SPIKING

RUN 01 PERCENT RECOVERIES[1]

	Train A			Train B[2]			Train C			Train D		
Compound	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery
d_5-pyridine	2837	3930	72	---	---	---	3268	4062	80	2875	3769	76
d_8-toluene	326	914	36	---	---	---	598	872	69	410	864	47
d_5-chlorobenzene	116	165	70	---	---	---	146	157	93	87	158	55
d_{10}-o-xylene	866	890	97	---	---	---	1029	838	123	490	835	59
d_2-tetrachloroethane	91	159	58	---	---	---	109	175	62	57	135	42
RUN 03 PERCENT RECOVERIES												
d_5-pyridine	3151	3930	80	---[3]	---	---	3281	4062	81	3367	3769	89
d_8-toluene	774	914	85	---	---	---	781	872	90	677	864	78
d_5-chlorobenzene	135	165	82	---	---	---	154	157	98	136	158	86
d_{10}-o-xylene	907	890	102	---	---	---	898	838	107	768	835	92
d_2-tetrachloroethane	68	159	43	---	---	---	79	175	45	79	135	59
RUN 04 PERCENT RECOVERIES												
d_5-pyridine	2378	3951	60	2284	4018	57	2481	4174	59	2724	4081	67
d_8-toluene	768	1009	76	698	1014	69	829	1007	82	774	993	78
d_5-chlorobenzene	133	180	74	130	180	72	168	198	85	205	196	105
d_{10}-o-xylene	856	966	89	848	954	89	971	957	101	1039	919	113
d_2-tetrachloroethane	70	83	84	68	84	81	88	100	88	128	95	135

---

[1] All values corrected for surrogate recoveries.

[2] Probe broken during Run 1, Train B.

[3] Sample went to dryness during concentration; no compounds recovered.

TABLE D-3. Continued

Compound	Train A			Train B			Train C			Train D		
	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery	ug Found	ug Spiked	Percent Recovery
RUN 05 PERCENT RECOVERIES												
d_5-pyridine	3427	3951	87	1953	4018	49	2848	4174	68	3520	4081	86
d_8-toluene	685	1009	68	822	1014	81	955	1007	95	1105	993	111
d_5-chlorobenzene	116	180	64	141	180	78	175	198	88	184	196	94
d_{10}-*o*-xylene	836	966	87	977	954	102	947	957	99	983	919	107
d_2-tetrachloroethane	52	83	63	56	84	67	86	100	86	84	95	88
RUN 08 PERCENT RECOVERIES												
d_5-pyridine	2318	4269	54	2943	4208	70	5038	4830	104	5065	4830	105
d_8-toluene	934	985	95	954	964	99	1161	1040	111	1174	1040	113
d_5-chlorobenzene	174	182	96	173	176	98	171	199	86	199	199	100
d_{10}-*o*-xylene	937	940	100	924	913	101	1050	1080	97	1068	1080	99
d_2-tetrachloroethane	94	82	114	92	86	106	87	101	86	92	101	91
RUN 09 PERCENT RECOVERIES												
d_5-pyridine	3587	4269	84	4215	4208	100	4560	4830	94	4135	4830	86
d_8-toluene	773	985	78	819	964	85	698	1040	67	737	1040	71
d_5-chlorobenzene	167	182	92	166	176	94	126	199	63	140	199	70
d_{10}-*o*-xylene	999	940	106	978	913	107	839	1080	78	862	1080	80
d_2-tetrachloroethane	118	82	144	116	86	135	56	101	55	83	101	82

control samples were used to adjust the test compound recoveries for the control samples. The same technique for adjustment of values was used for all of the field samples. The collected mass of pyridine was not adjusted because the compound was not retained on the XAD-2® resin, but was collected in the back-half (aqueous) of the Semi-VOST train. Adjusted values for all of the field data are shown in Table D-3.

The final analysis performed each day was a control sample prepared by Radian. The results of the daily analysis of this control sample are tabulated and summarized in Appendix E.

Some representative chromatograms for the field samples are shown in Figures D-1 through D-4. Samples Run 10A Front and Run 10A Back (Figures D-1 and D-2) were spiked in the field using the dynamic spiking system. Samples Run 10D Front and 10D Back were not spiked. An inspection of the chromatograms shows that the number of eluted compounds is small. The major peaks of all of the chromatograms beyond an approximately 5-minute retention time are all attributed to mass spectrometric quantitation standards, surrogate compounds, or low levels of unspiked non-isotopically labeled test compounds. Runs 10A Front and 10A Back also show peaks in this retention window which are attributed to isotopically labeled compounds spiked through the dynamic spiking system.

Figure D-1. Chromatogram of Run 10A, Front Half. Note that the chromatogram is not complex. All of the major peaks beyond scan 400 (approximately 5 minutes retention time) are attributed to mass spectrometric quantitation compounds, surrogate compounds, or low levels of unspiked compounds which are not isotopically labeled. Run 10A was spiked in the field using the dynamic spiking system.

```
MIDRIC                                   DATA: 5AAC531 #1        SCANS    1 TO 2000
08/30/86 22:36:00                        CALI: 5AAC531 #2
SAMPLE: SEMIVOST 10A FRONT
CONDS.: 875V
RANGE: G   1,2000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

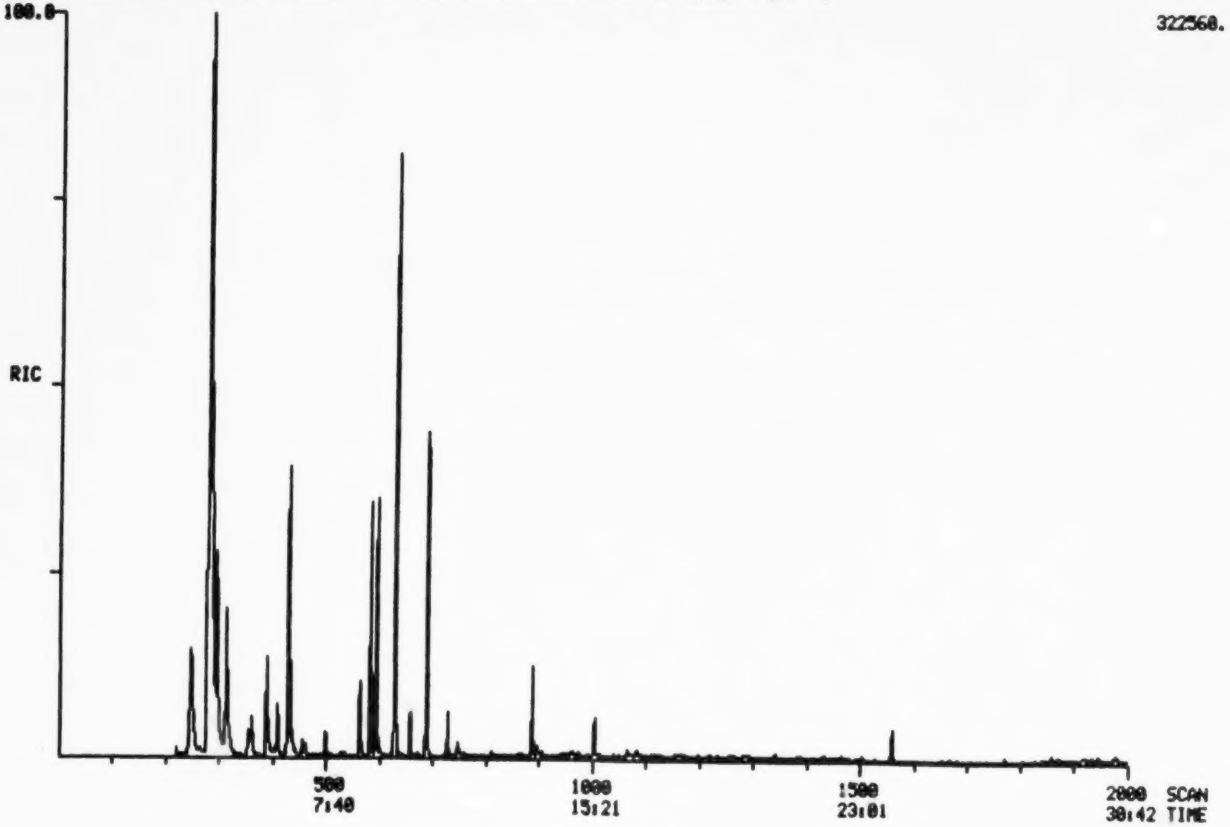


Figure D-2. Chromatogram of Run 10A, Back Half. Note that the chromatogram is not complex. All of the major peaks beyond scan 400 (approximately 5 minutes retention time) are attributed to mass spectrometric quantitation compounds, surrogate compounds, or low levels of unspiked compounds which are not isotopically labeled. Run 10A was spiked in the field using the dynamic spiking system.

```
MIDRIC                                   DATA: 5AAC532 01        SCANS    1 TO 2000
08/30/86 23:16:00                        CALI: 5AAC532 02
SAMPLE: SEMIVOST 10A BACK
CONDS.: 875V
RANGE: G   1,2000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

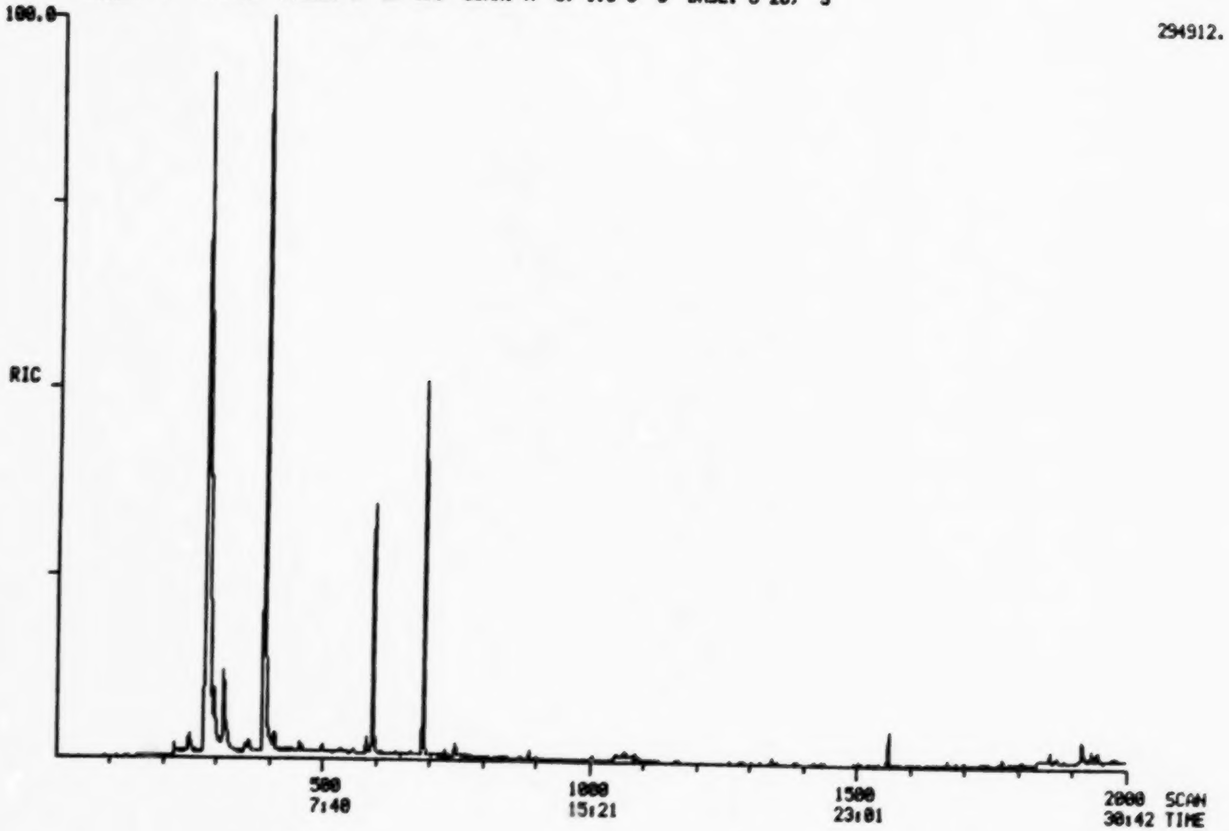


Figure D-3. Chromatogram of Run 10D, Front Half. Note that the chromatogram is not complex. All of the major peaks beyond scan 400 (approximately 5 minutes retention time) are attributed to mass spectrometric quantitation compounds, surrogate compounds, or low levels of unspiked compounds which are not isotopically labeled. Run 10D was not spiked in the field.

```
MIDRIC
08/30/86 15:58:00             DATA: 5AAC527 #1        SCANS    1 TO 2000
SAMPLE: SEMIVOST 10 D FRONT   CALI: 5AAC528 #2
CONDS.: 875V
RANGE: G   1,2000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

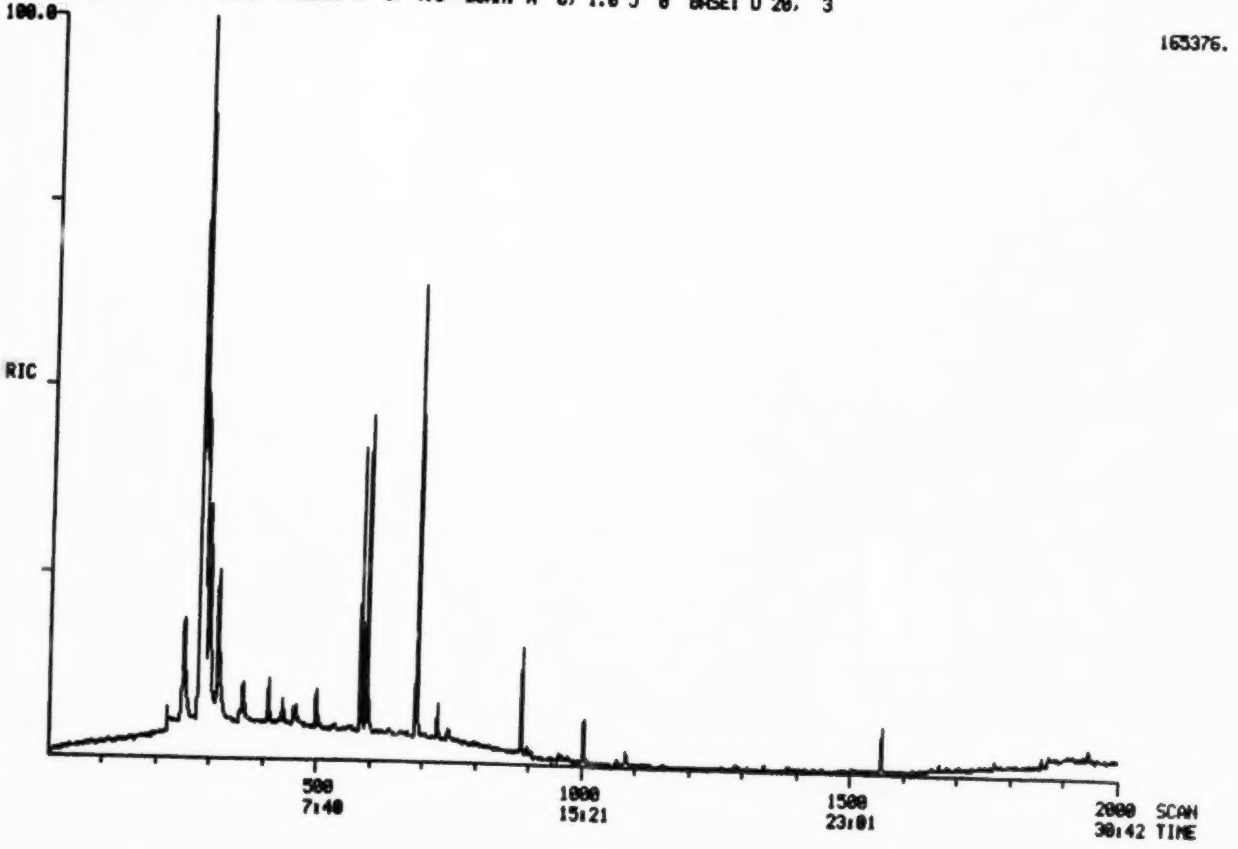
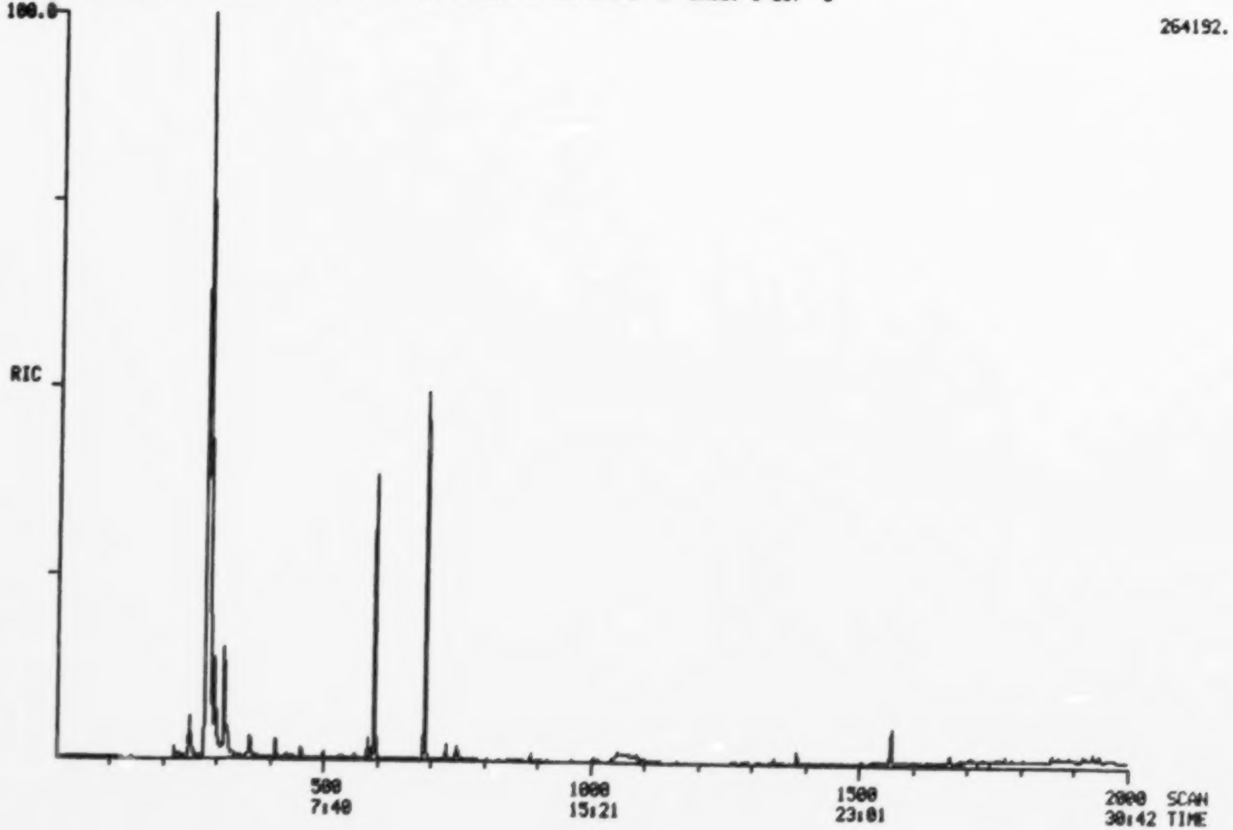


Figure D-4. Chromatogram of Run 10D, Back Half. Note that the chromatogram is not complex. All of the major peaks beyond scan 400 (approximately 5 minutes retention time) are attributed to mass spectrometric quantitation compounds, surrogate compounds, or low levels of unspiked compounds which are not isotopically labeled. Run 10D was not spiked in the field.

```
MIDRIC                                  DATA: 5AAC530 01        SCANS    1 TO 2000
08/30/86 21:58:00                       CALI: 5AAC530 02
SAMPLE: SEMIVOST 10D BACK
CONDS.: 075V
RANGE: G   1,2000  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```



APPENDIX E

QUALITY ASSURANCE/QUALITY CONTROL

The quality assurance (QA) activities used for the field test evaluation of the Semi-VOST sampling and analysis methodology are detailed in the Quality Assurance Project Plan for that field test[1]. The QA project plan was designed according to the guidelines proposed in the EPA draft document "Guidelines and Specifications for Preparing Quality Assurance Project Plans", QAMS-005/80.

In this appendix, the following quality control/quality assurance (QA/QC) data are presented: (1) a summary of field quality control procedures; and (2) data from the analyses of check samples prepared by the Research Triangle Institute. All data are presented for: (1) control charts for the daily analyses of calibration standards used to calculate recoveries of surrogates and quantities of compounds; (2) daily tuning data from the gas chromatograph/mass spectrometer/data system for decafluorotriphenylphosphine, the compound used as a tuning standard; and (3) data from the column performance standard, analyzed weekly to monitor possible deterioration of the chromatographic column.

QUALITY CONTROL DURING FIELD ACTIVITIES

Calibrations of Field Equipment

The gas meters, thermocouples, temperature gauges, and probe nozzles were calibrated as described in Section 3.4.2 of EPA document 600/4-77-027b, Quality Assurance Handbook for Air Pollution Measurement Systems. The type S pitot tube assembly was calibrated using the procedure in Section 3.1.2 of EPA Reference Method 2.

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(1) Field Test Evaluation of the Semi-VOST Sampling and Analysis Methodology at a Waste Incineration Facility, (Section 5.0 Quality Assurance/Quality Control) Radian Corporation, June 12, 1986.

The spiking system was designed by Radian Corporation and was calibrated by following the procedure outlined in the QA/QC plan. The dynamic spiking system was calibrated in the laboratory prior to the field test and in the field just prior to testing, immediately following testing and at any time the test was interrupted for any reason.

Testing Procedures

In order to maintain the validity of the field data, several quality control steps were implemented. They included leak checks, consistency of clean-up procedures, monitoring of the flow, temperature and vacuum gauges throughout the testing period, noting abnormalities during testing, and complete documentation of data.

One of the criteria used to judge the validity of a sampling run was to obtain a flow rate of less than 9.4 mL/s during leak checks of the sampling trains. In all cases, a satisfactory leak check was obtained before the test, at any break in testing for necessary filter changes, and at the completion of the test. During Run 07 and Run 10, the filters were changed due to the accumulation of particulate.

All clean-up procedures were carried out by one person to eliminate any variance between trains due to individual technique differences. Solvent blanks were taken on a regular basis during the field testing.

A flow rate of (0.5 CFM) through the train was required throughout the testing period. This was an approximation of the isokinetic rate in the variable stack flow.

After the first 5 test runs, the feed was composed of approximately 50% to 80% aqueous waste, resulting in an inordinate amount of aqueous condensate in the sampling train. The condensate was removed from the first impinger during the test runs through a siphoning tube incorporated into the design of the system. This process did not have an effect on the leak checks.

Liquid feed samples were collected daily for analysis if necessary.

QUALITY CONTROL DURING LABORATORY ACTIVITIES

Analysis of Check Samples Supplied by the Research Triangle Institute

The Research Triangle Institute (RTI) prepared seven check samples for analysis by the Radian Research Triangle Park Laboratories. These samples consisted of three XAD-2® modules which had been spiked with known quantities of pyridine, toluene, chlorobenzene, 1,1,2,2-tetrachloroethane, and o-xylene, and four XAD-2® modules which were blanks. Two of the spiked modules and two of the blank modules were sent to the field as "trip blanks." The remaining spiked module and two blank modules were reserved in the laboratory. One of the blank "trip blanks" was invalidated during sample preparation. The results of the analyses are shown in Table E-1. Before extracting samples, a deuterated spike of the test compounds was added, as was a deuterated surrogate to check recovery efficiency. All test compounds were corrected for surrogate recoveries. Mean surrogate recoveries were as follows:

d_{10}-ethylbenzene	80.2%
d_5-phenol	82.5%
d_5-nitrobenzene	82.0%
d_8-naphthalene	73.5%

Table E-2 shows the comparison of the observed values with the expected levels of the five compounds spiked onto the XAD-2® by RTI. Average percent bias values ranged from -1.84 percent to -8.90 percent when referenced to the RTI values. Average percent bias was -4.68. This is excellent agreement and shows that the recovery of a range of organic compounds from XAD-2® using the Semi-VOST methodology is favorable. The small average percent bias lends validity to the experimental results determined by the Semi-VOST method.

Daily Calibration of the GC/MS System

An initial calibration of the GC/MS system was performed using duplicate injections at each of five concentration levels to generate a response factor data base. Over the period of time necessary to analyze all samples, three data bases were generated. The generation of these data bases is discussed in Appendix D. The protocol for the analysis of field samples required the analysis of a calibration standard and a control sample each day, one at the beginning of the day and one at the end of the day. Two presentations of the results of the daily calibration analyses are given -- control charts for the individual

TABLE E-1. RTI CONTROL SAMPLES, THEORETICAL LOADING

Compound	C351 RTI BLANK XAD 12547	C352 RTI SPIKE 12543 (1 of 3)	C353 RTI SPIKE 12544 (2 of 3)	C354 RTI SPIKE 13245 (3 of 3)	C355 RTI BLANK 13202	C356 RTI BLANK 13201
Surrogate Compounds, % Recoveries						
d_{10}-ethylbenzene	77	85	79	78	82	80
d_5-phenol	77	84	83	79	88	84
d_5-nitrobenzene	69	80	82	78	95	88
d_8-naphthalene	62	75	78	75	78	73
Spiked Compounds, % Recoveries+						
d_5-pyridine	111	119	106	106	104	93
d_8-toluene	79	86	72	76	68	69
d_5-chlorobenzene	67	73	64	70	65	63
d_{10}-o-xylene	96	99	91	95	91	87
d_2-tetrachloroethane	54	65	62	63	60	58
Test Compounds, Total ug*†						
pyridine	8.7	1924	1924	1905	7.9	ND
toluene	7.7	850	822	824	1.9	ND
chlorobenzene	2.6	216	214	221	ND	ND
o-xylene	ND	818	829	820	ND	ND
tetrachloroethane	ND	146	147	143	ND	ND

*Values corrected for Surrogate Recovery.

+Spiked by Radian.

†Spiked by RTI.

TABLE E-2. RESULTS OF ANALYSIS OF RTI CONTROL SAMPLES

Compound	Expected Level, ug	Determined Levels, ug[1] (1)	(2)	(3)	Mean Observed Level (ug/module)	% bias
Pyridine	1,963.8	1924	1942	1905	1,923.7	-2.04
Toluene	866.9	850	822	824	832.0	-4.03
Chlorobenzene	221.1	216	214	221	217.0	-1.84
1,1,2,2-Tetrachloroethane	159.5	146	147	143	145.3	-8.90
o-Xylene	880.2	818	829	820	822.3	-6.50
Dodecane	748.8	---	---	---	---	---
				Overall Average % Bias		-4.68

[1] Values corrected for Surrogate Recovery.

[2] $\% \text{ Bias} = \frac{\text{mean observed} - \text{Expected Level}}{\text{Expected Level}} \times 100$

compounds and a tabular summary of the values. Figures E1 through E48 are the control charts with the appropriate data base shown at the top. The mean response factor from the 10-point data base is shown as the mean value in the control charts. Around that mean, the standard deviation of the values in the data base is 1σ, 2σ, and 3σ. Nearly all of the points obtained in the daily analyses of calibration samples are within the 3σ range of the control charts. Table E-3 presents the same information in tabular form. The value of the response factor calculated for each ion of each compound is shown with the date for the analysis. Table E-4 gives a tabular summary of the daily control sample analysis. An evaluation of these two tables shows the excellent stability for the analytical instrument and entirely acceptable reproducibility of values for the response factors over the entire period of the analytical determination.

Daily Tuning Data for the GC/MS System

The compound decafluorotriphenylphosphine (DFTPP) was used as the daily tuning standard for the mass spectrometer. The criteria for acceptability of the tune of the mass spectrometer are shown in Table E-5. No analysis was performed until the instrument had satisfied tuning criteria every day.

The data obtained for the daily analyses of DFTPP are also shown in Table E-5. The table shows the ions specified in the criteria, with a comparison between observed values and the specified values. A set of information showing a plotted mass spectrum obtained daily from the analysis of DFTPP, and a set of data including a list of the masses and intensities obtained for this compound will be made available upon request. An inspection of the values obtained for analysis of DFTPP also illustrates the excellent stability of the mass spectrometer during this study.

ANALYSIS OF THE COLUMN PERFORMANCE SOLUTION

The column performance solution consists of a mixture of compounds which are intended to test the condition of the chromatographic column in order to decide whether column maintenance should be performed on a given chromatographic column. Critical parameters are resolution, separation number, and peak asymmetry. The calculation and values obtained are described below.

RESPONSE FACTOR CONTROL CHARTS

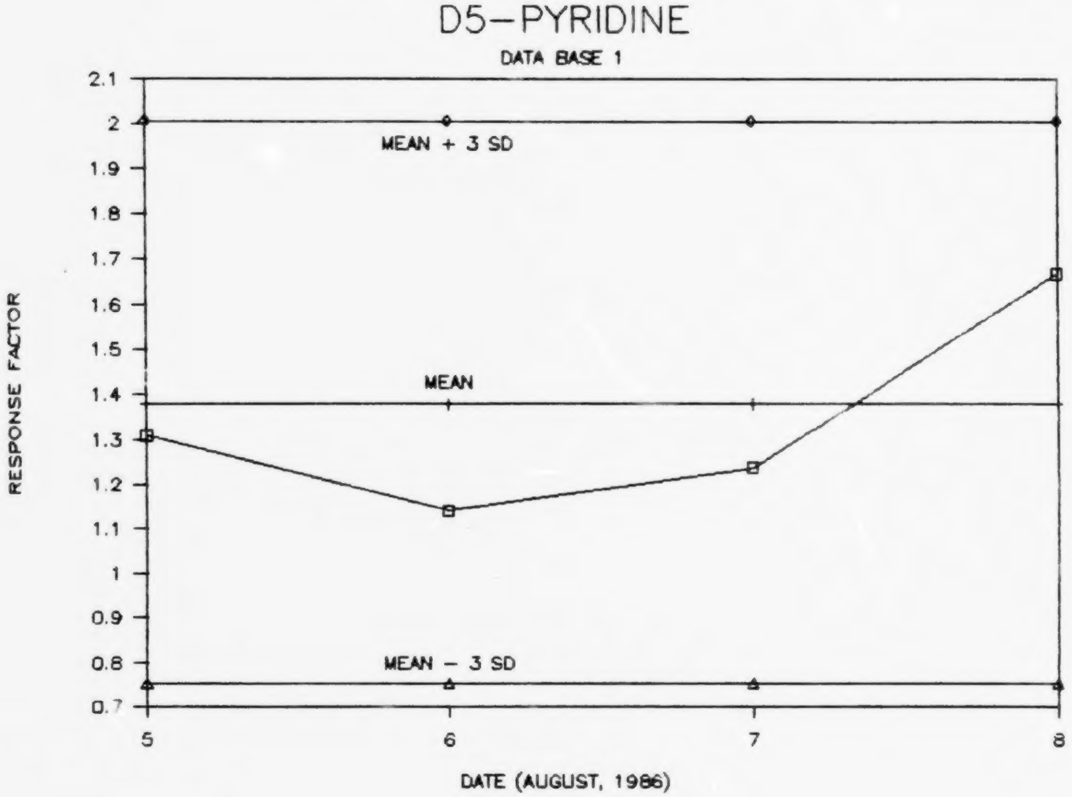

D5-PYRIDINE
DATA BASE 1
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
MEAN + 3 SD
MEAN
MEAN - 3 SD
5
6
7
8
DATE (AUGUST, 1986)

Figure E-1

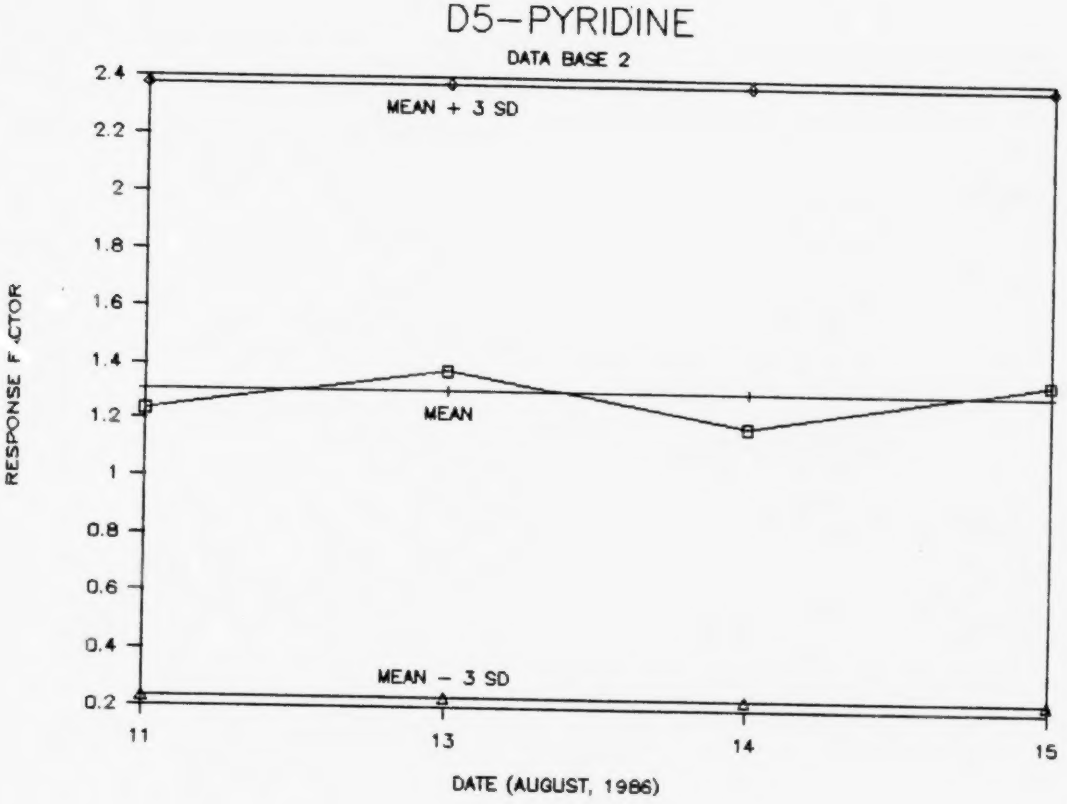

D5–PYRIDINE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
11
13
14
15
DATE (AUGUST, 1986)

Figure E-2

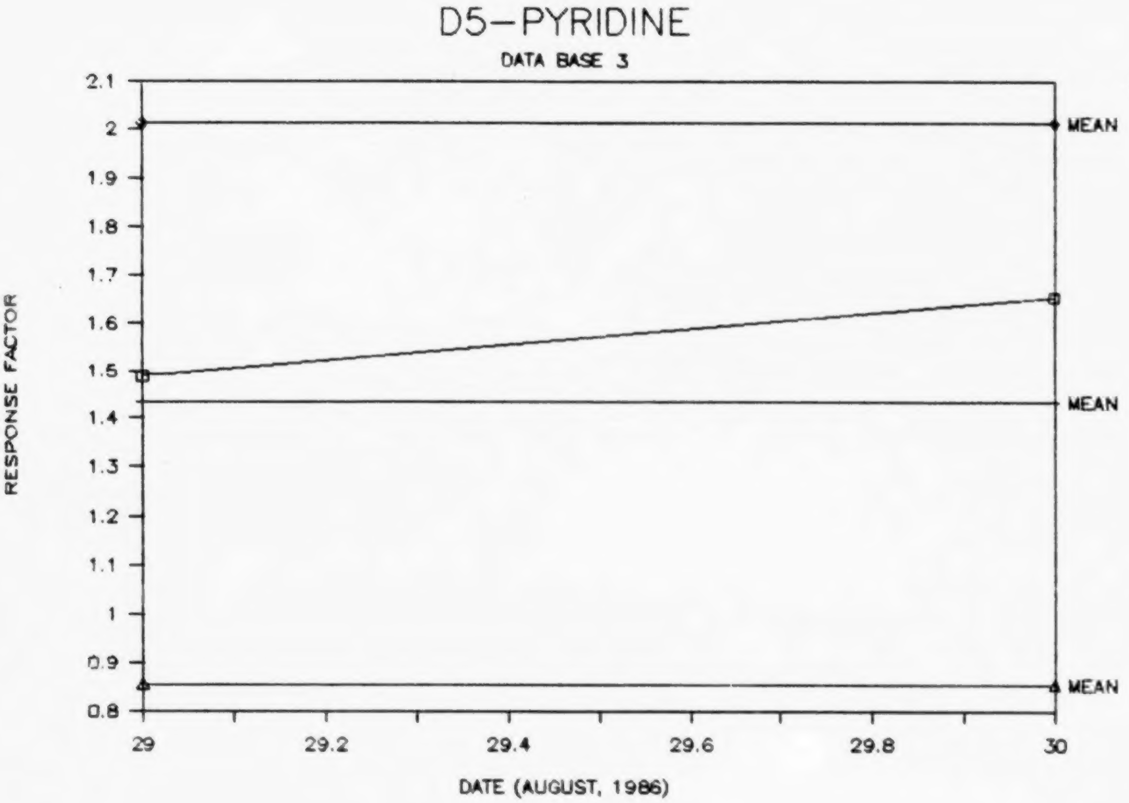

D5–PYRIDINE
DATA BASE 3
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)
MEAN
MEAN
MEAN

Figure E-3

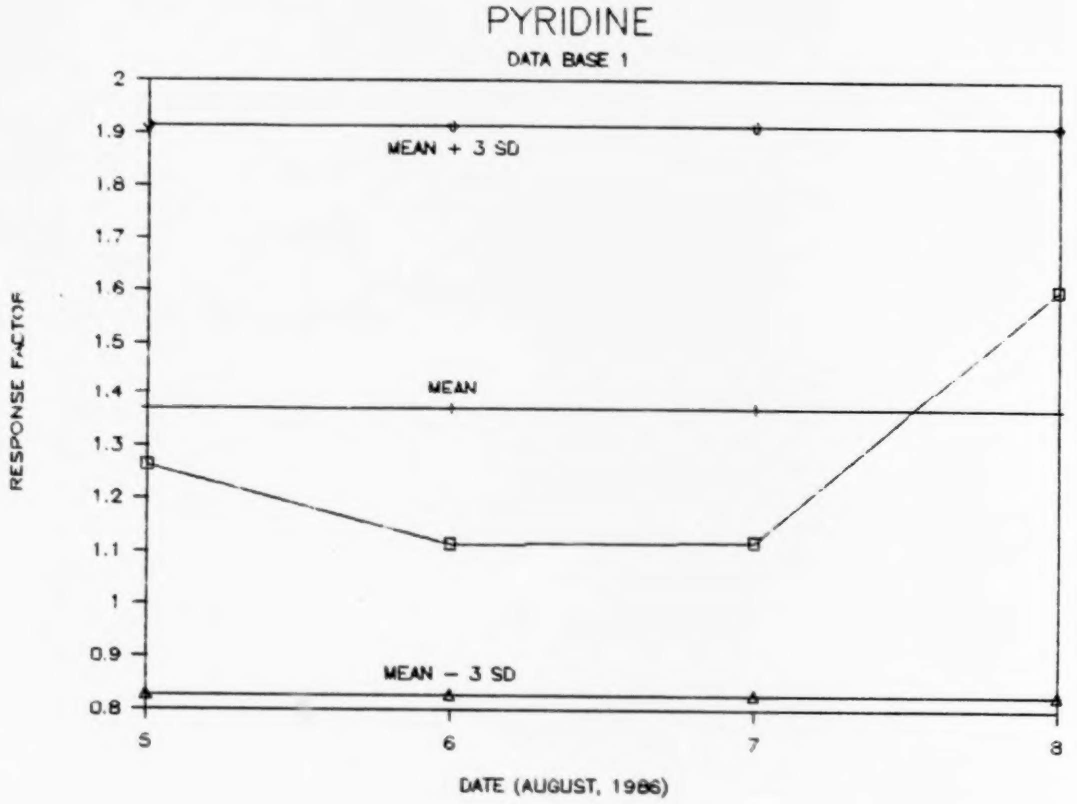

PYRIDINE
DATA BASE 1
RESPONSE FACTOR
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
MEAN + 3 SD
MEAN
MEAN – 3 SD
5
6
7
8
DATE (AUGUST, 1986)

Figure E-4

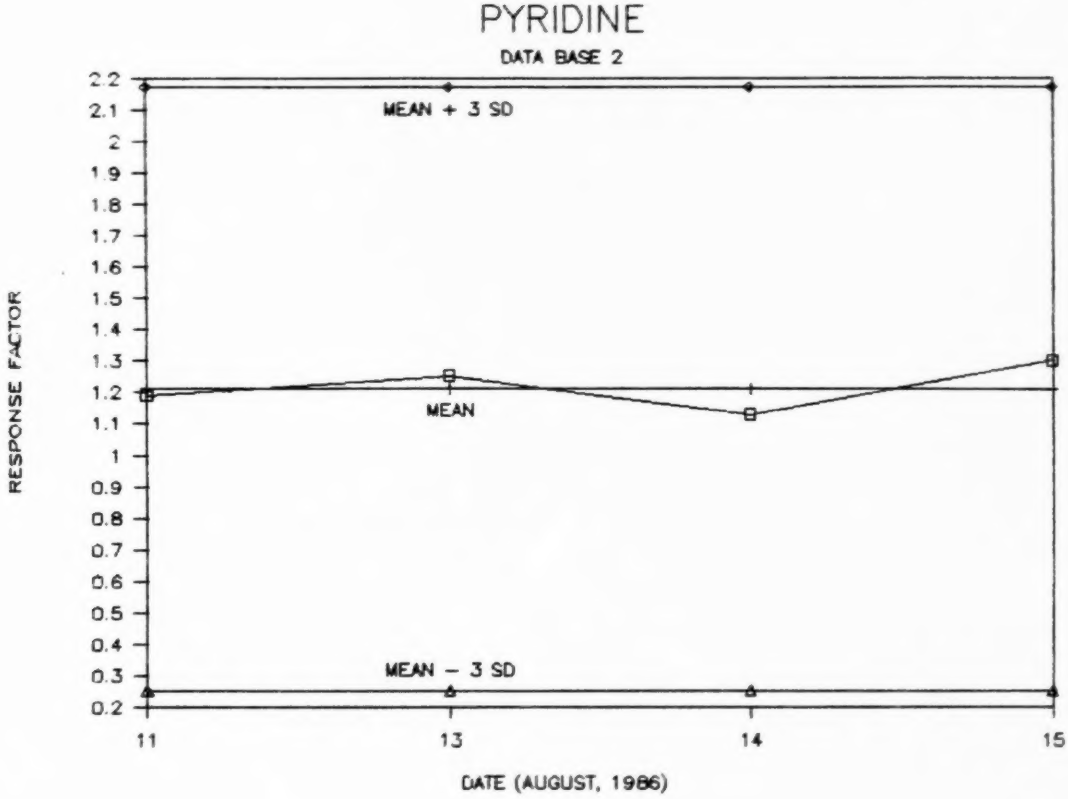
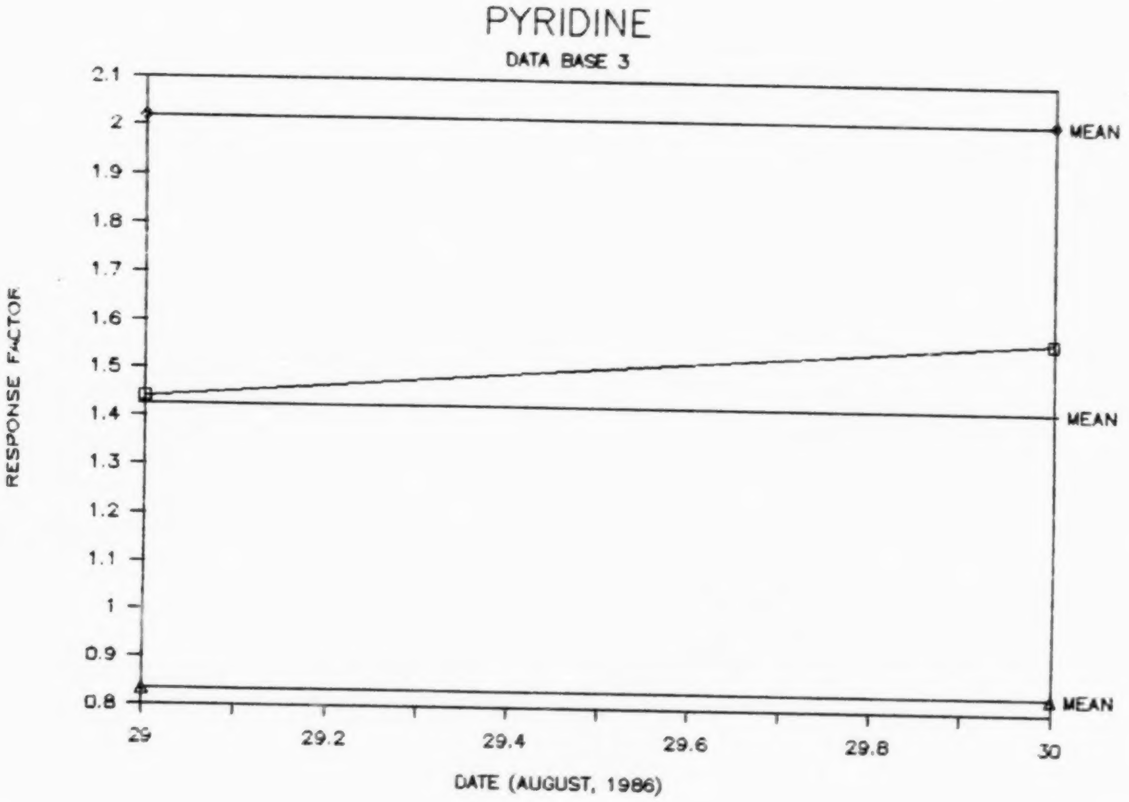

PYRIDINE
DATA BASE 2
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
RESPONSE FACTOR
MEAN + 3 SD
MEAN
MEAN − 3 SD
11
13
14
15
DATE (AUGUST, 1986)

Figure E-5



PYRIDINE
DATA BASE 3
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-6

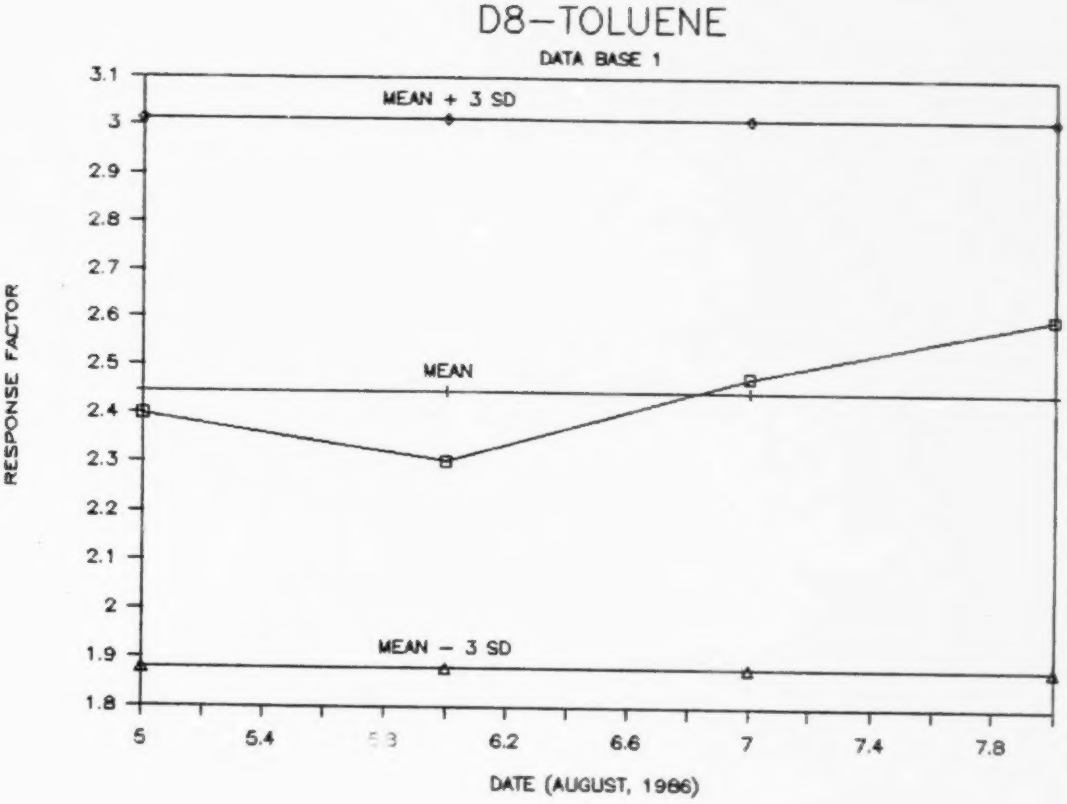

D8—TOLUENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN − 3 SD
RESPONSE FACTOR
3.1
3
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-7

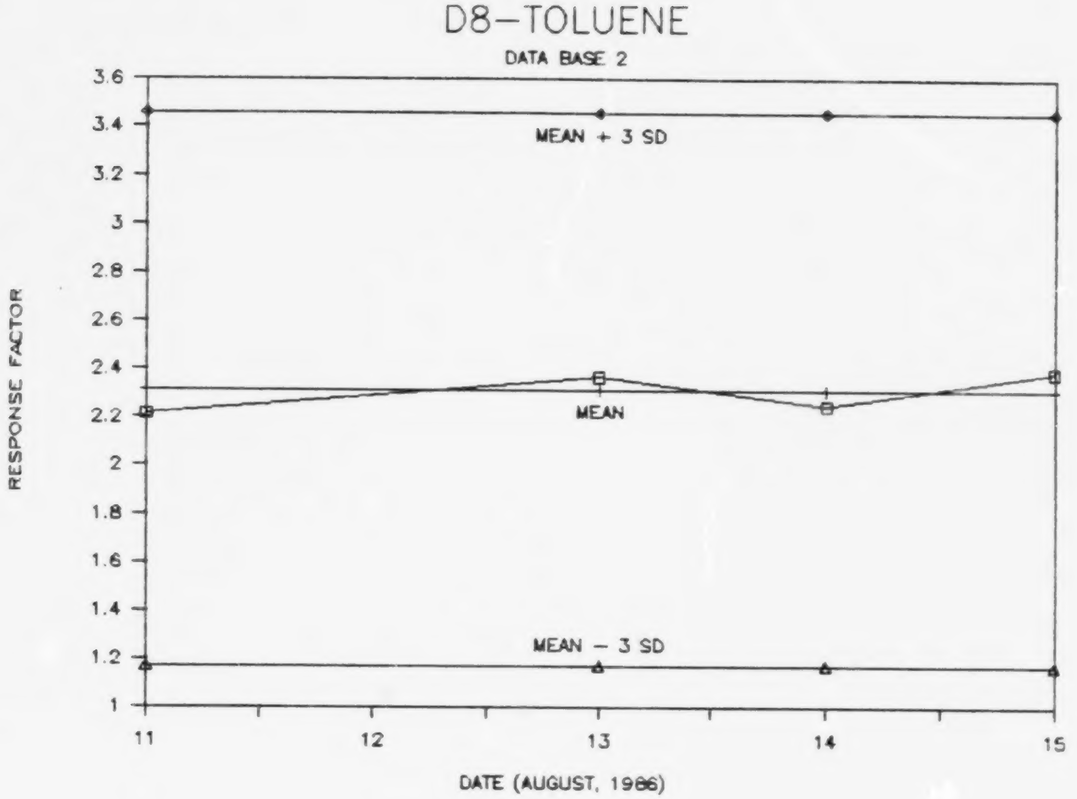

D8—TOLUENE
DATA BASE 2
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
RESPONSE FACTOR
MEAN + 3 SD
MEAN
MEAN — 3 SD
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-8

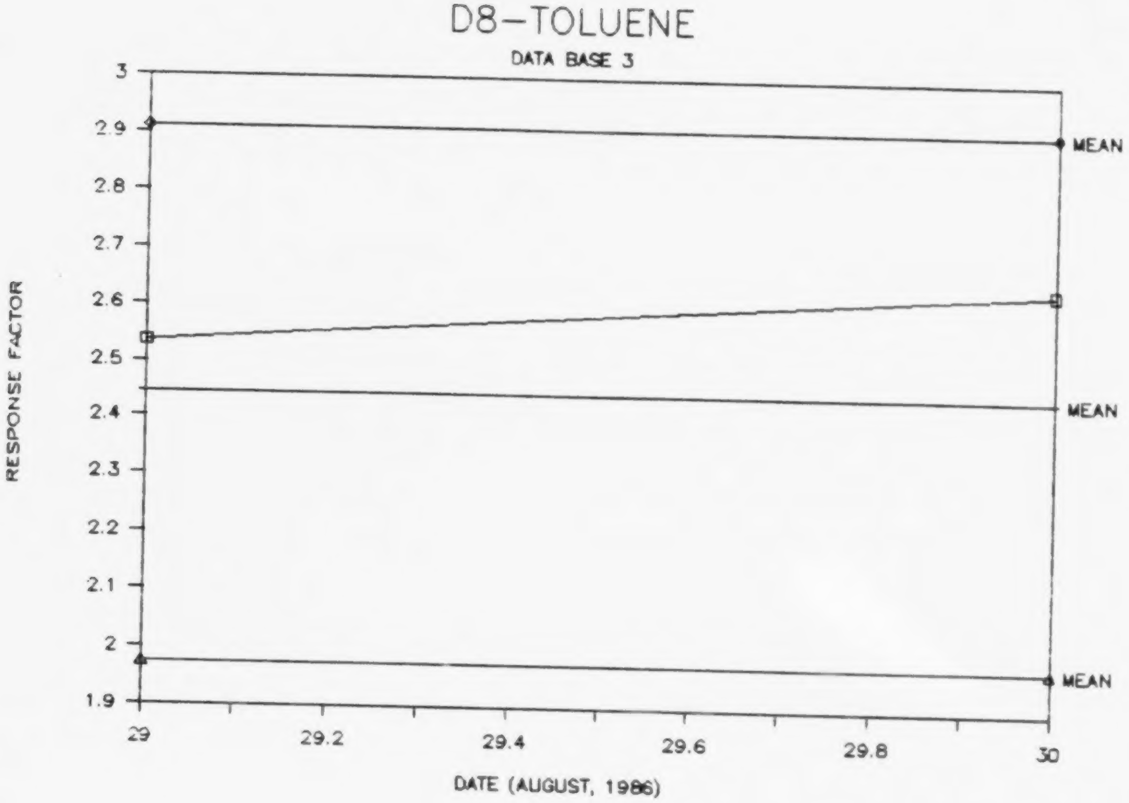

D8-TOLUENE
DATA BASE 3
RESPONSE FACTOR
3
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-9

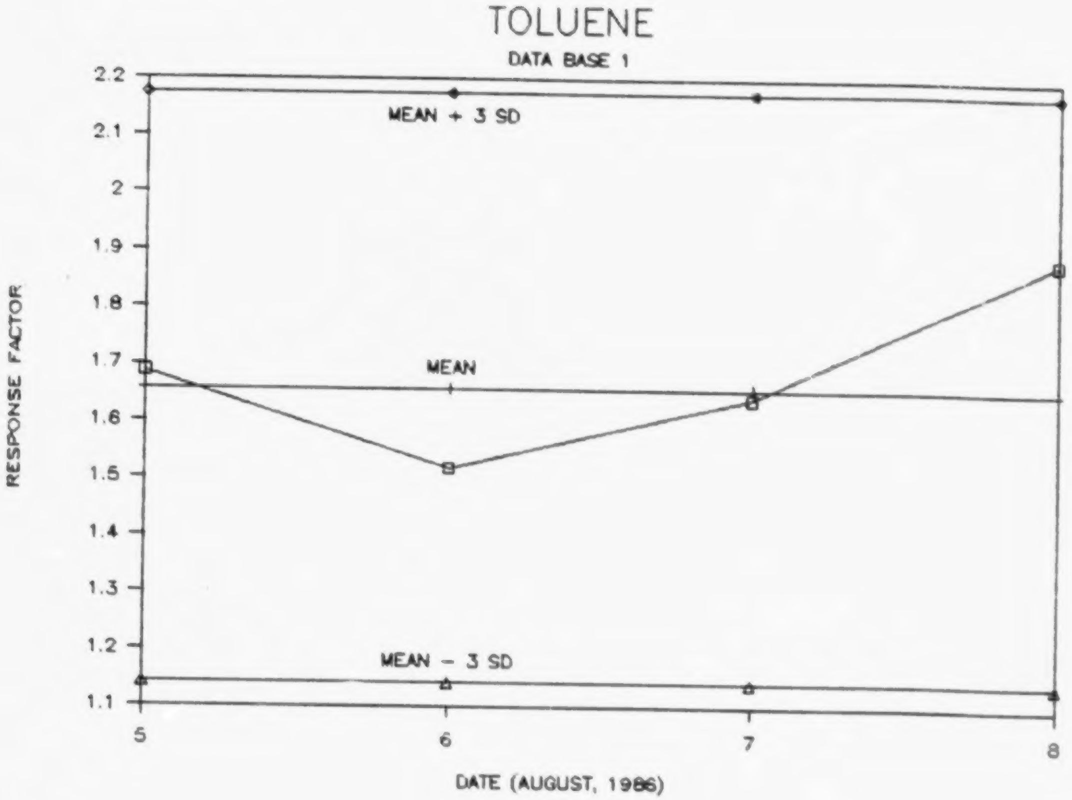

TOLUENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
5
6
7
8
DATE (AUGUST, 1986)

Figure E-10

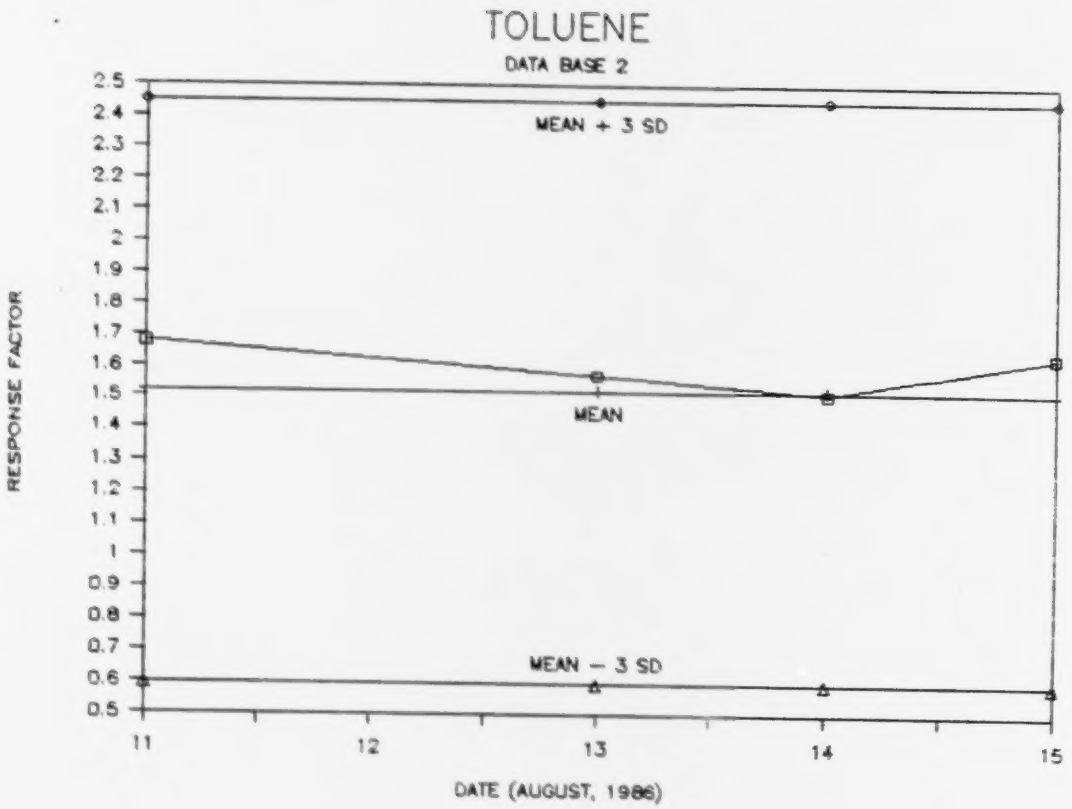

TOLUENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN − 3 SD
RESPONSE FACTOR
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-11

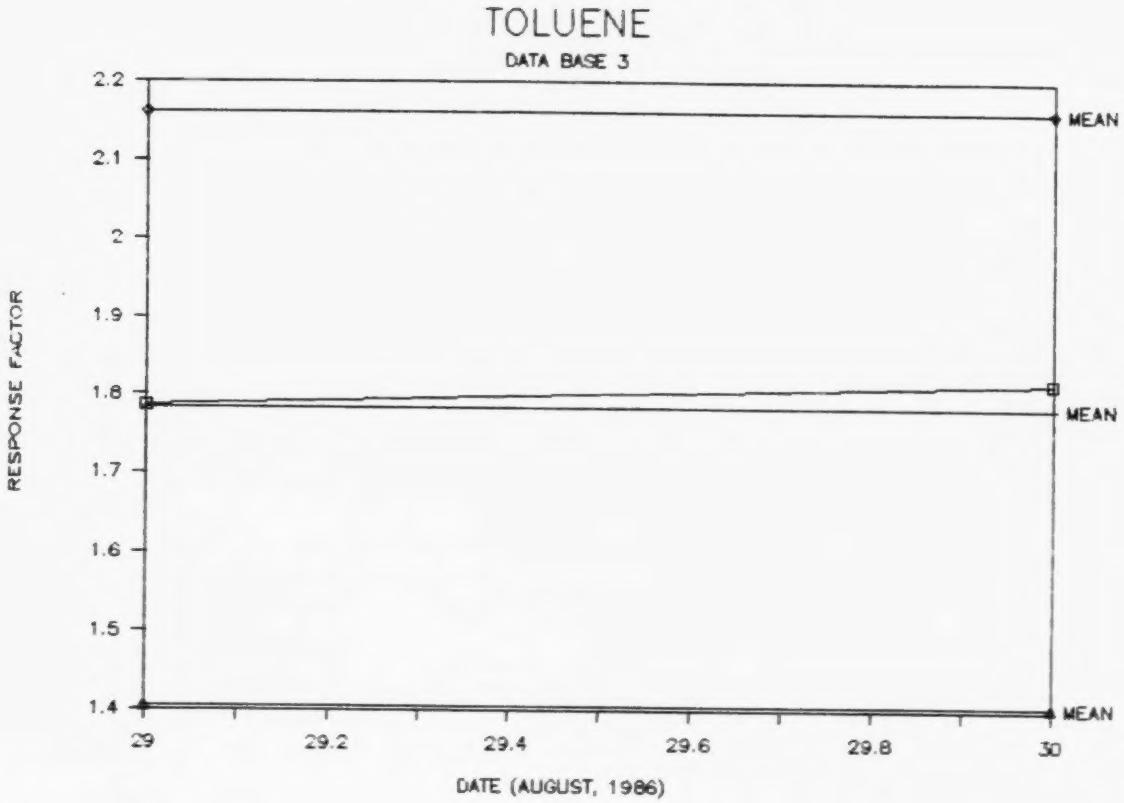

TOLUENE
DATA BASE 3
RESPONSE FACTOR
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)
MEAN
MEAN
MEAN

Figure E-12

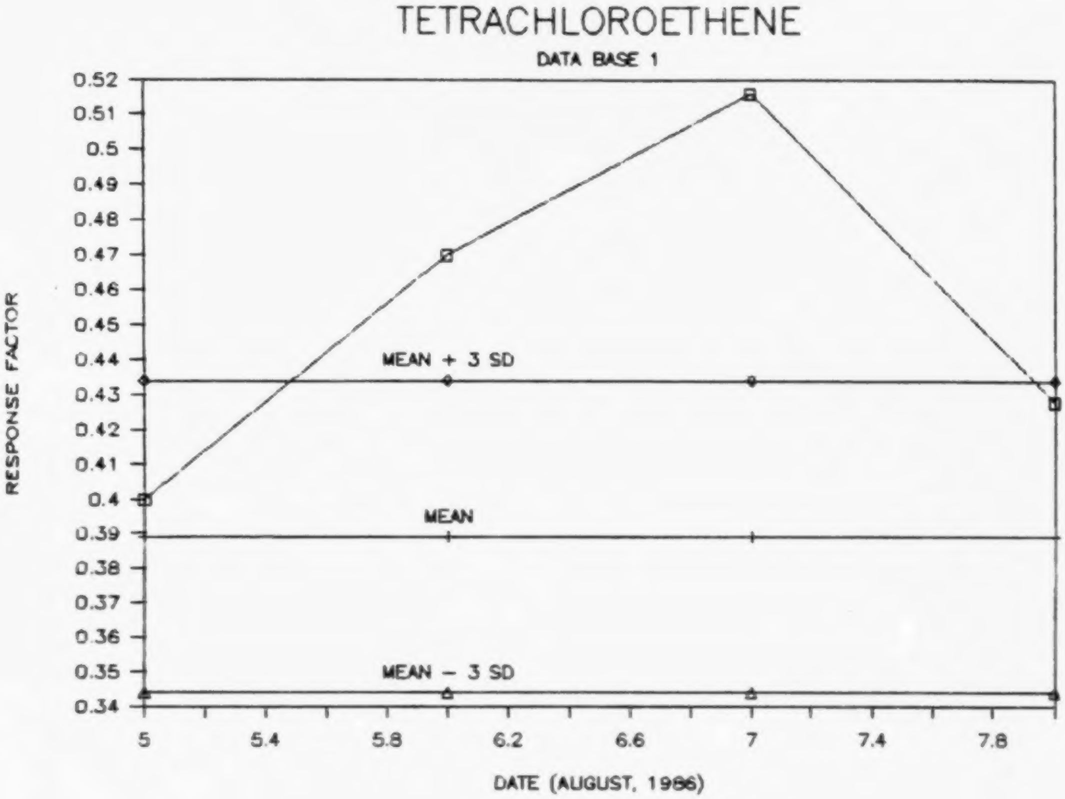

TETRACHLOROETHENE
DATA BASE 1
RESPONSE FACTOR
0.52
0.51
0.5
0.49
0.48
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.4
0.39
0.38
0.37
0.36
0.35
0.34
MEAN + 3 SD
MEAN
MEAN – 3 SD
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-13

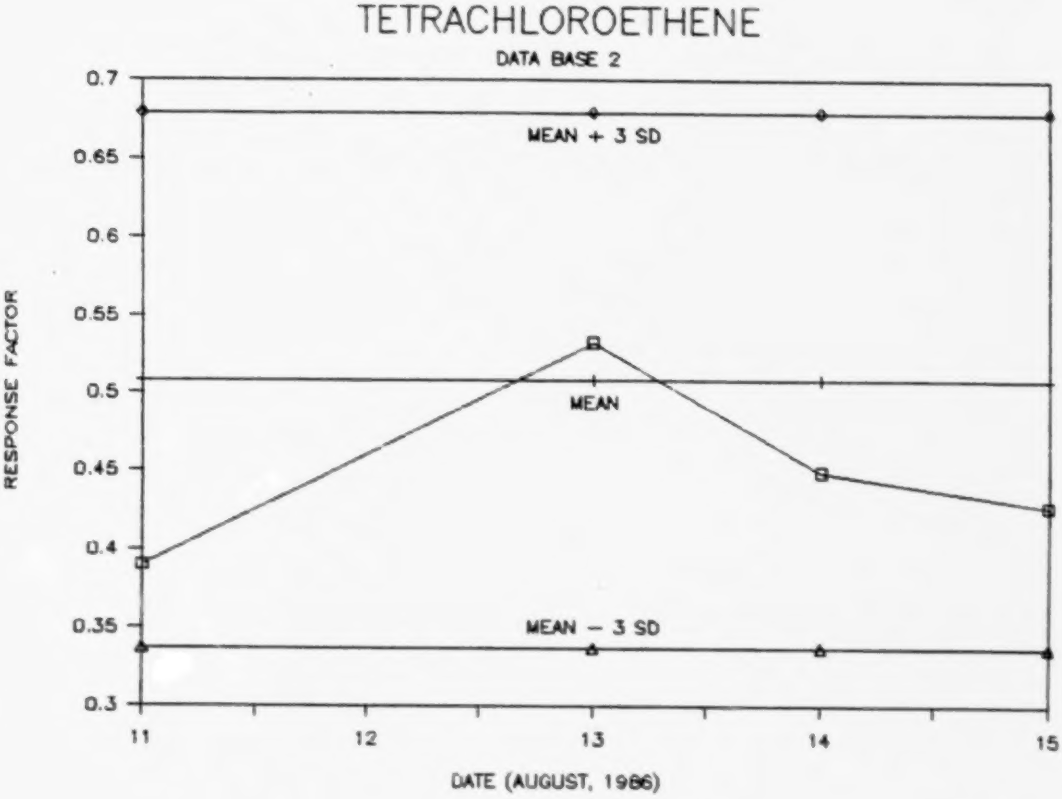

TETRACHLOROETHENE
DATA BASE 2
RESPONSE FACTOR
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
MEAN + 3 SD
MEAN
MEAN – 3 SD
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-14

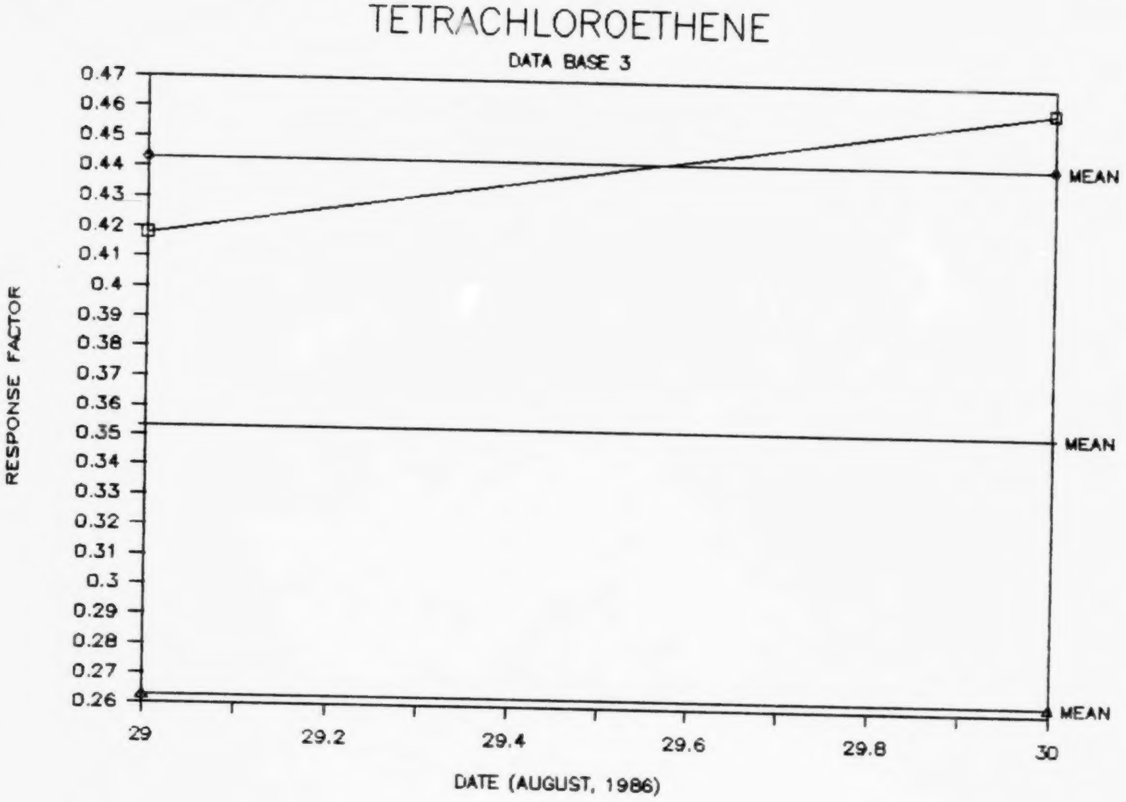

TETRACHLOROETHENE
DATA BASE 3
RESPONSE FACTOR
0.47
0.46
0.45
0.44
0.43
0.42
0.41
0.4
0.39
0.38
0.37
0.36
0.35
0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-15

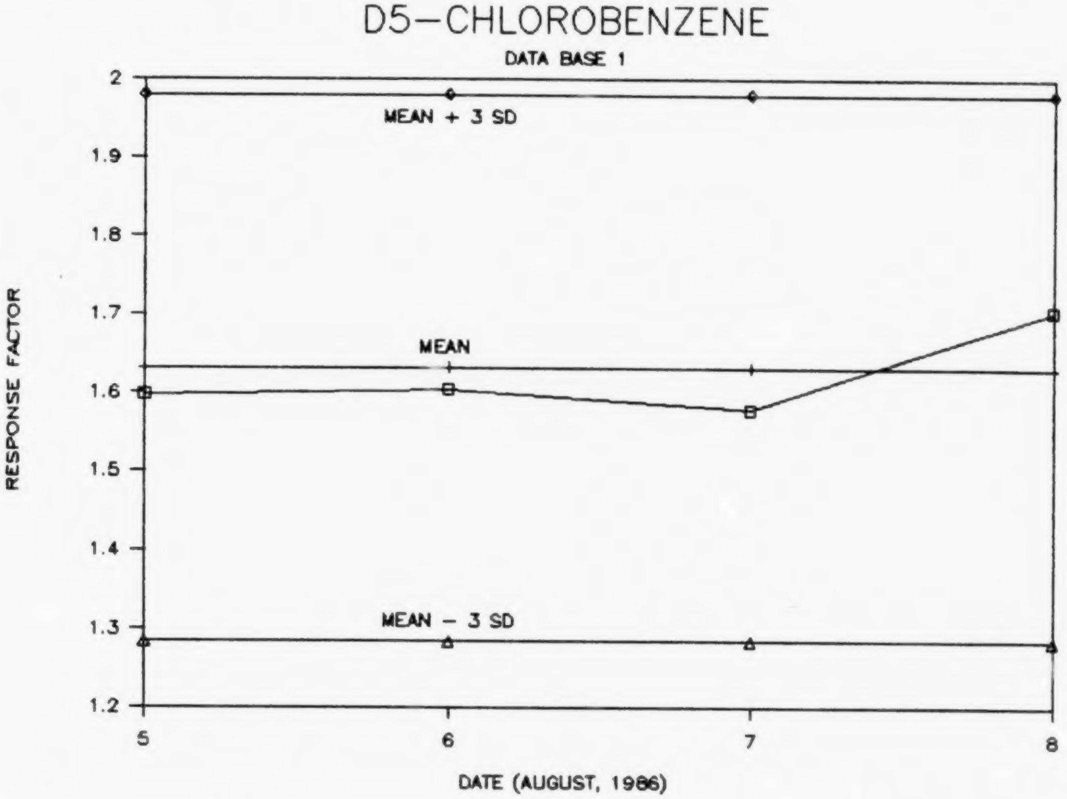

D5–CHLOROBENZENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
5
6
7
8
DATE (AUGUST, 1986)

Figure E-16

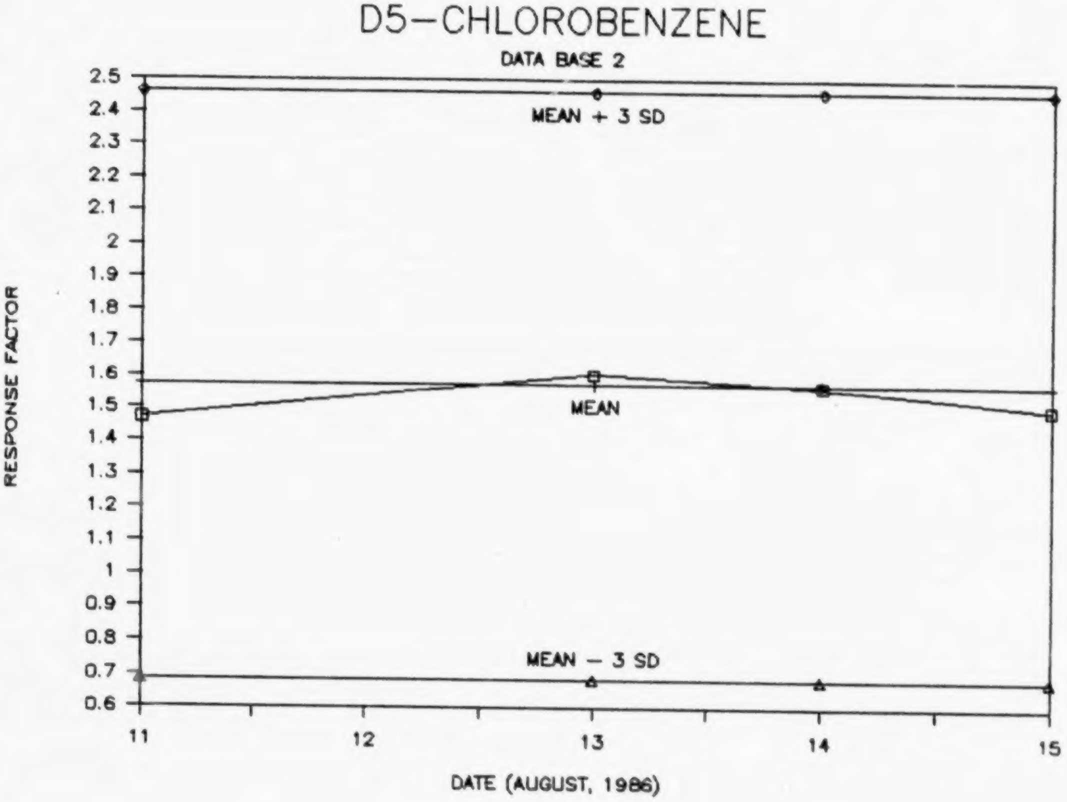
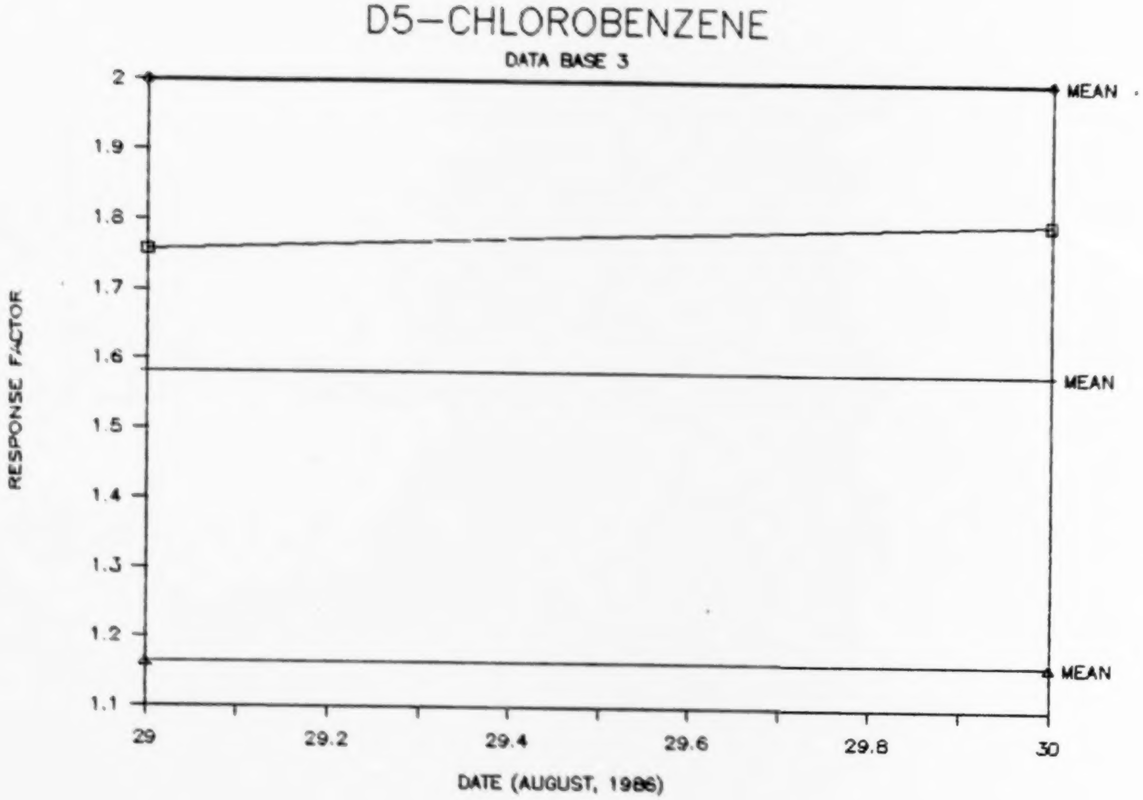

D5-CHLOROBENZENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN - 3 SD
RESPONSE FACTOR
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-17



D5—CHLOROBENZENE
DATA BASE 3
RESPONSE FACTOR
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-18

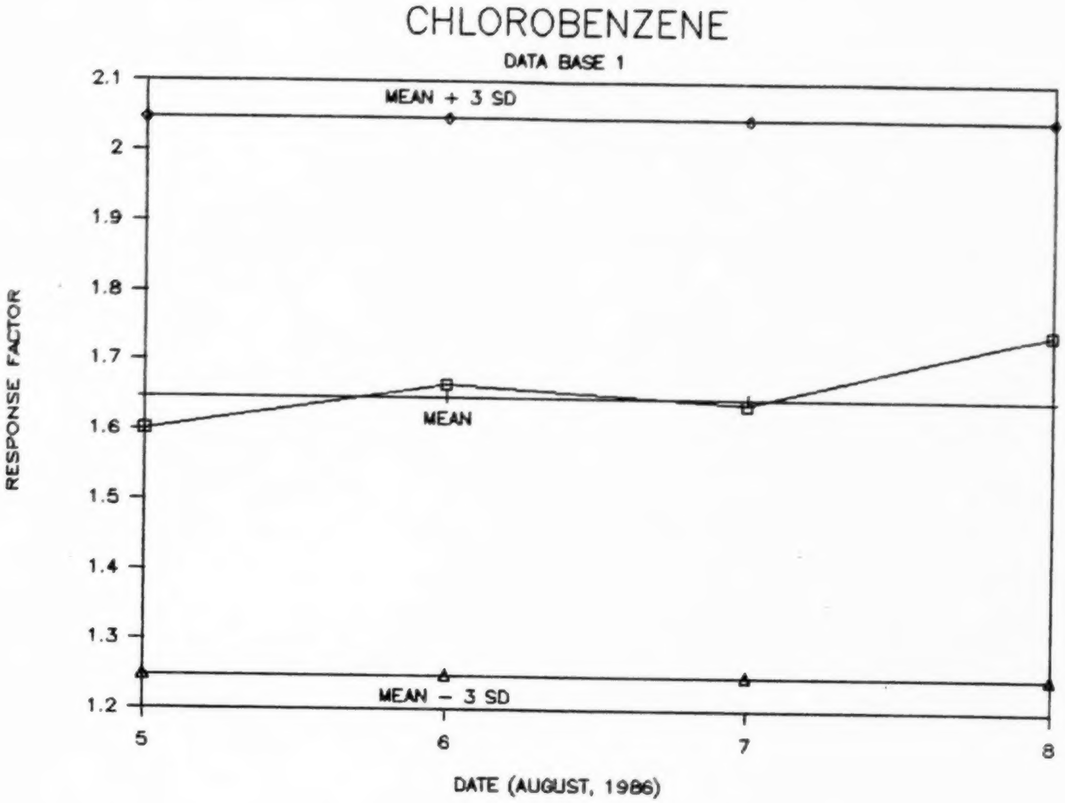

CHLOROBENZENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
5
6
7
8
DATE (AUGUST, 1986)

Figure E-19

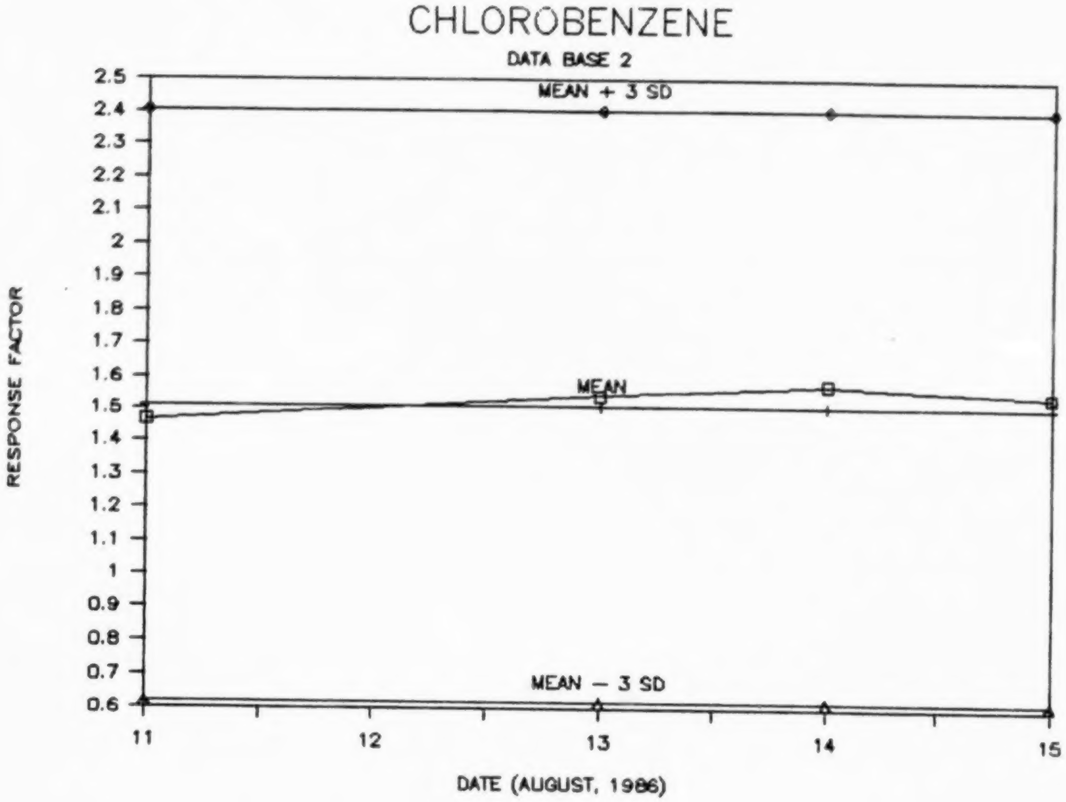

CHLOROBENZENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN — 3 SD
RESPONSE FACTOR
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-20

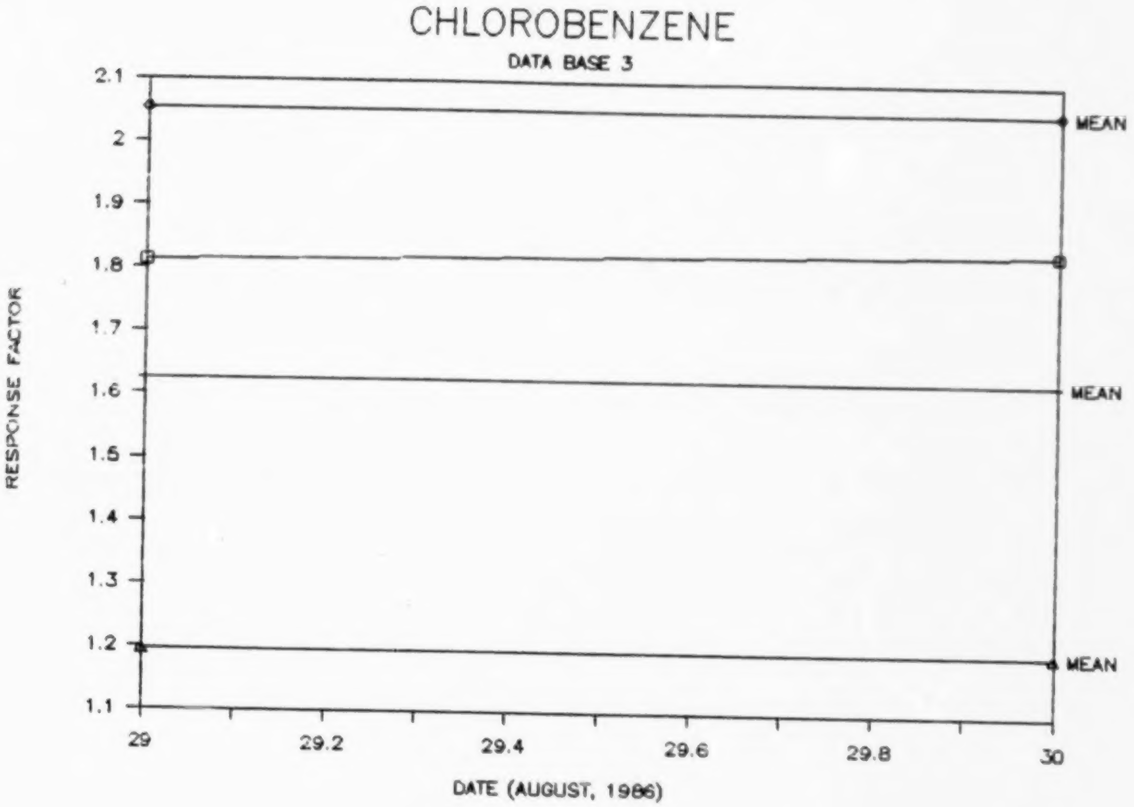

CHLOROBENZENE
DATA BASE 3
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)
MEAN
MEAN
MEAN

Figure E-21

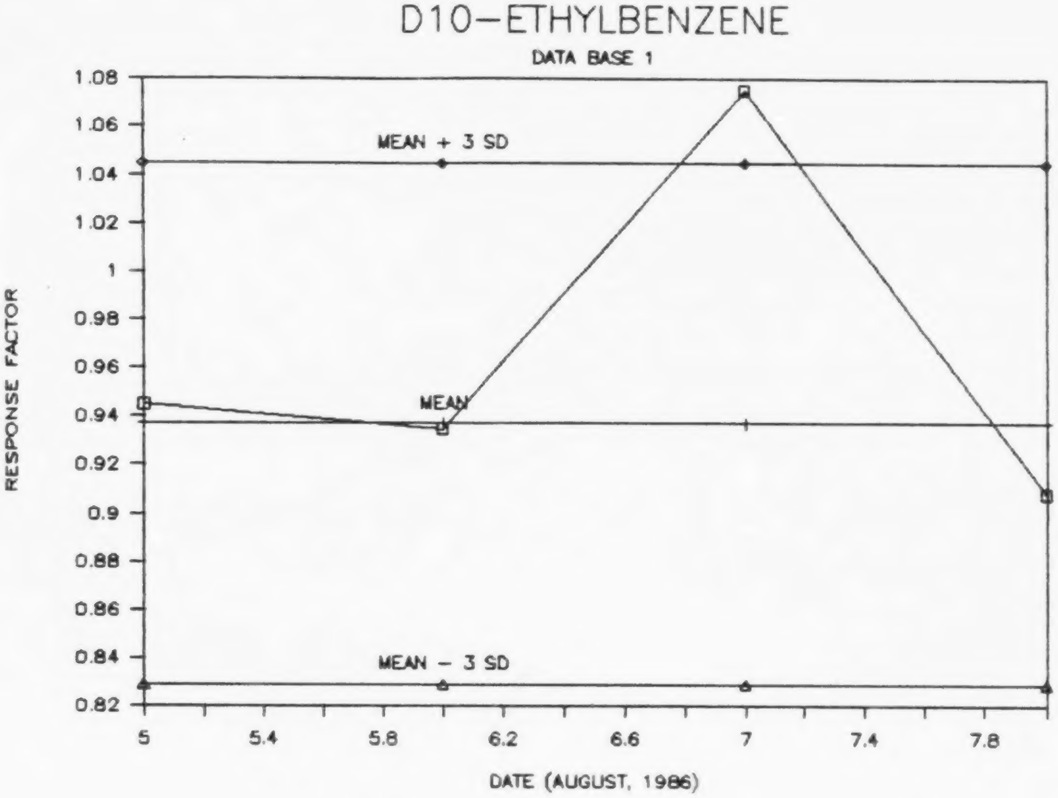

D10–ETHYLBENZENE
DATA BASE 1
RESPONSE FACTOR
1.08
1.06
1.04
1.02
1
0.98
0.96
0.94
0.92
0.9
0.88
0.86
0.84
0.82
MEAN + 3 SD
MEAN
MEAN – 3 SD
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-22

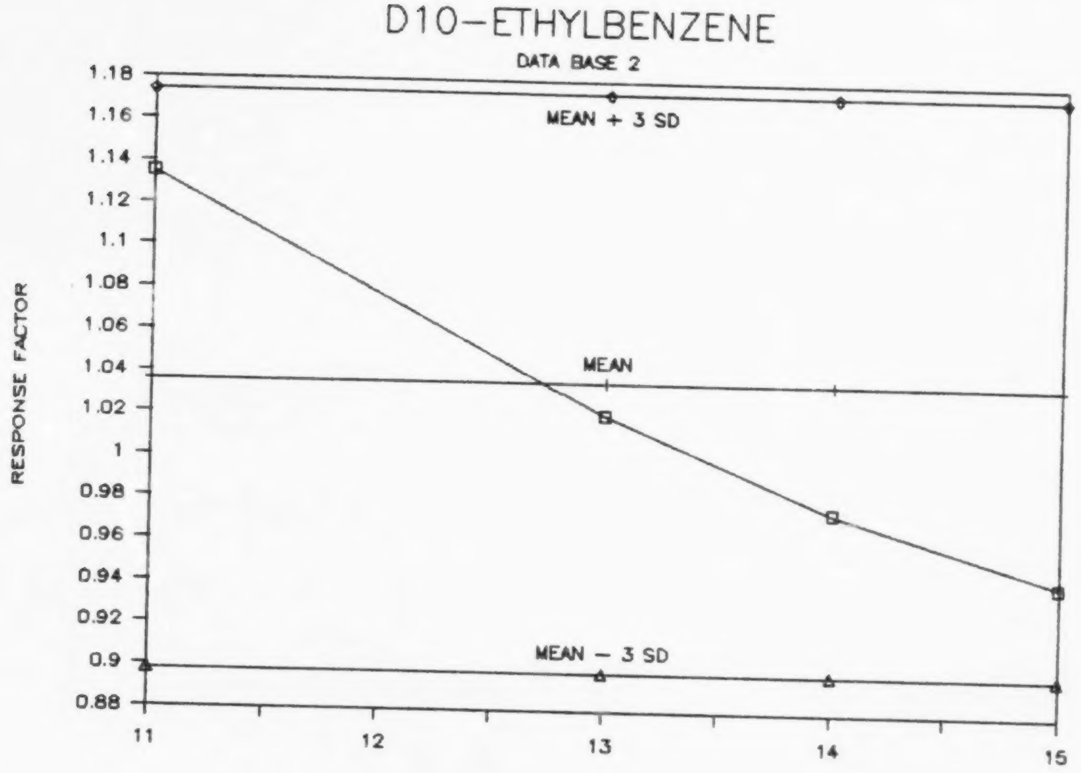

D10-ETHYLBENZENE
DATA BASE 2
RESPONSE FACTOR
1.18
1.16
1.14
1.12
1.1
1.08
1.06
1.04
1.02
1
0.98
0.96
0.94
0.92
0.9
0.88
MEAN + 3 SD
MEAN
MEAN - 3 SD
11
12
13
14
15

Figure E-23

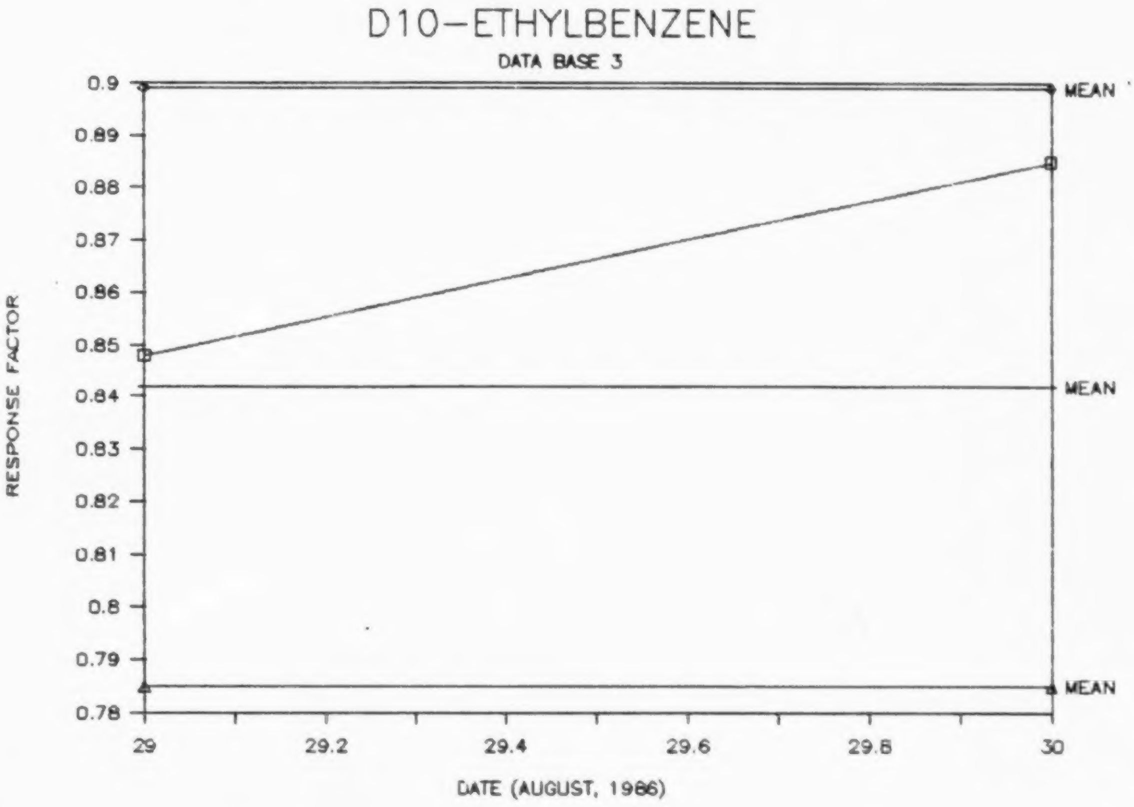

D10-ETHYLBENZENE
DATA BASE 3
RESPONSE FACTOR
0.9
0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
0.8
0.79
0.78
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-24

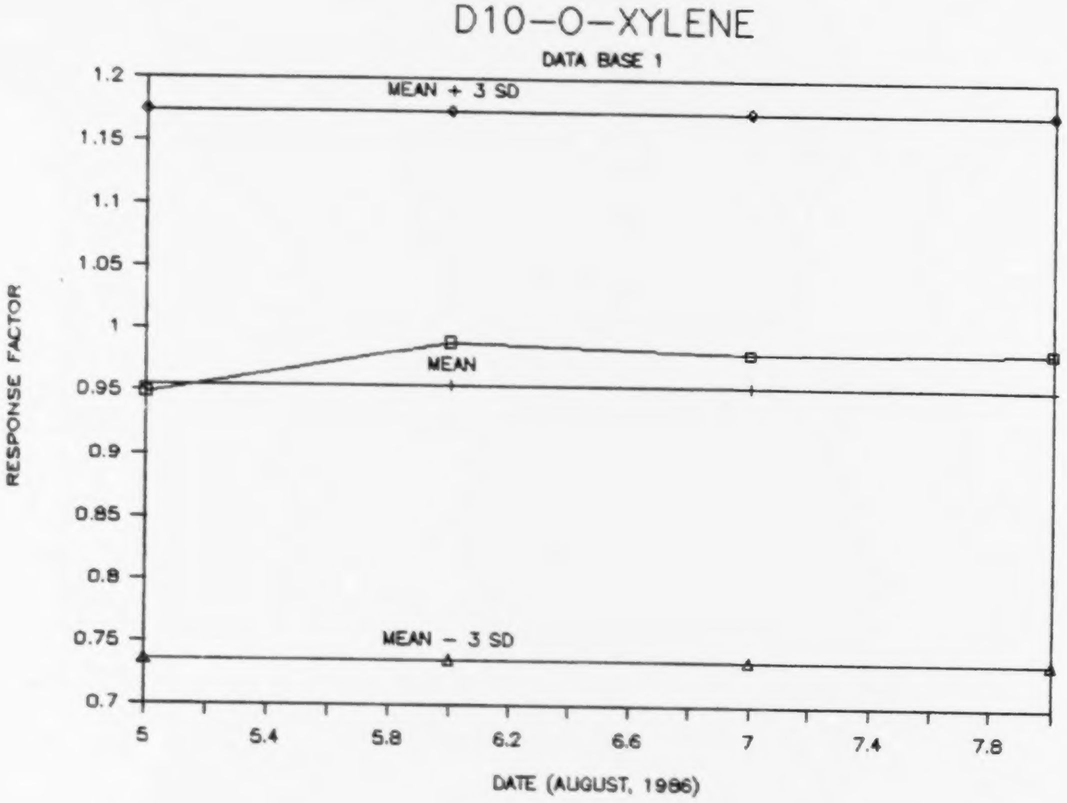

D10–O–XYLENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-25

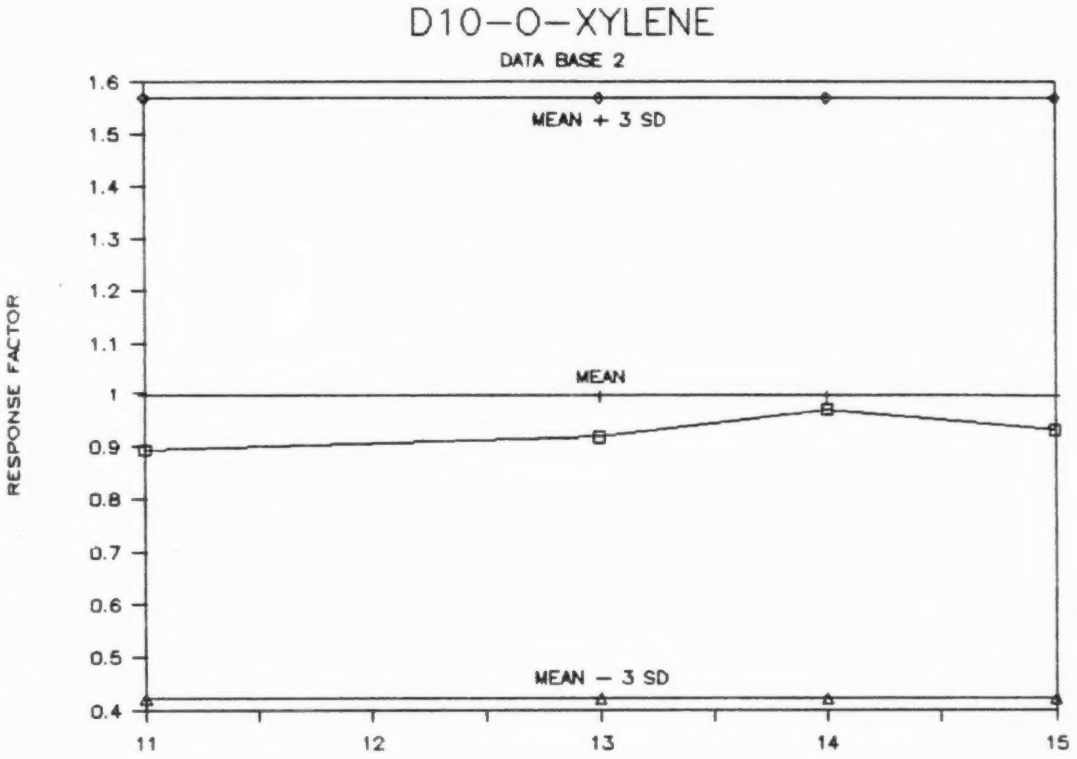

D10-O-XYLENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN − 3 SD
RESPONSE FACTOR
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
11
12
13
14
15

Figure E-26

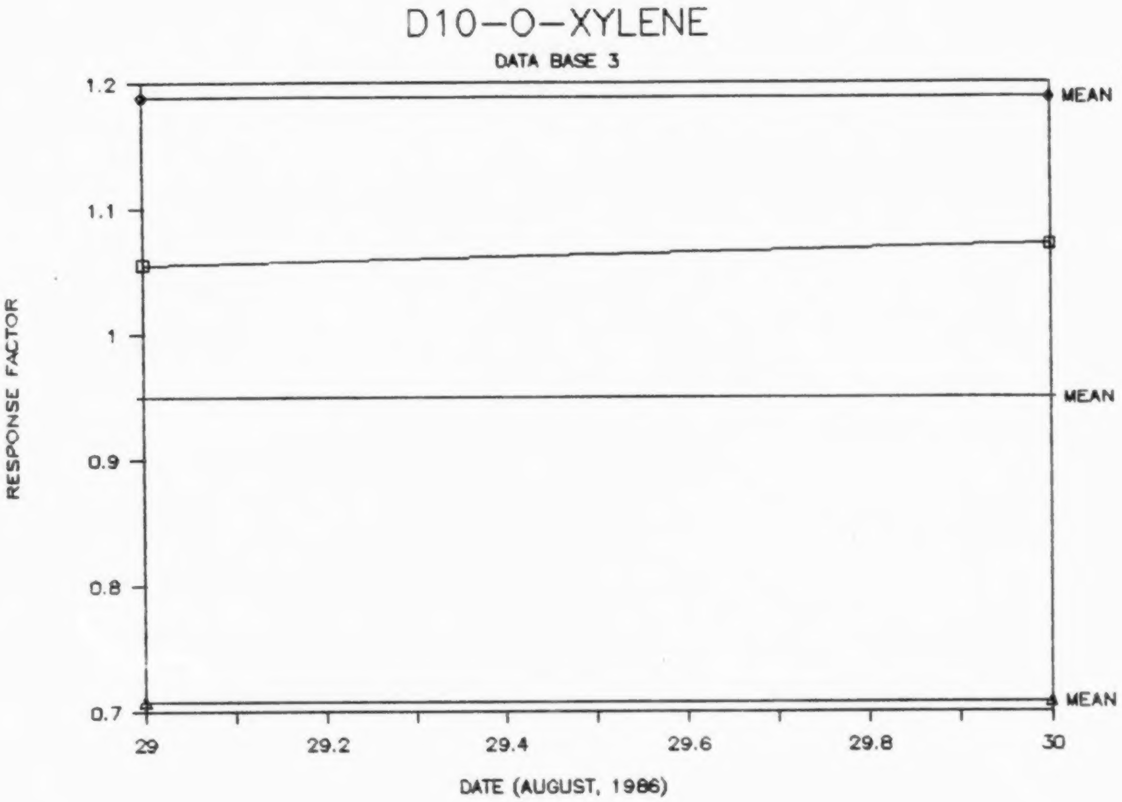

D10-O-XYLENE
DATA BASE 3
1.2
1.1
1
0.9
0.8
0.7
RESPONSE FACTOR
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-27

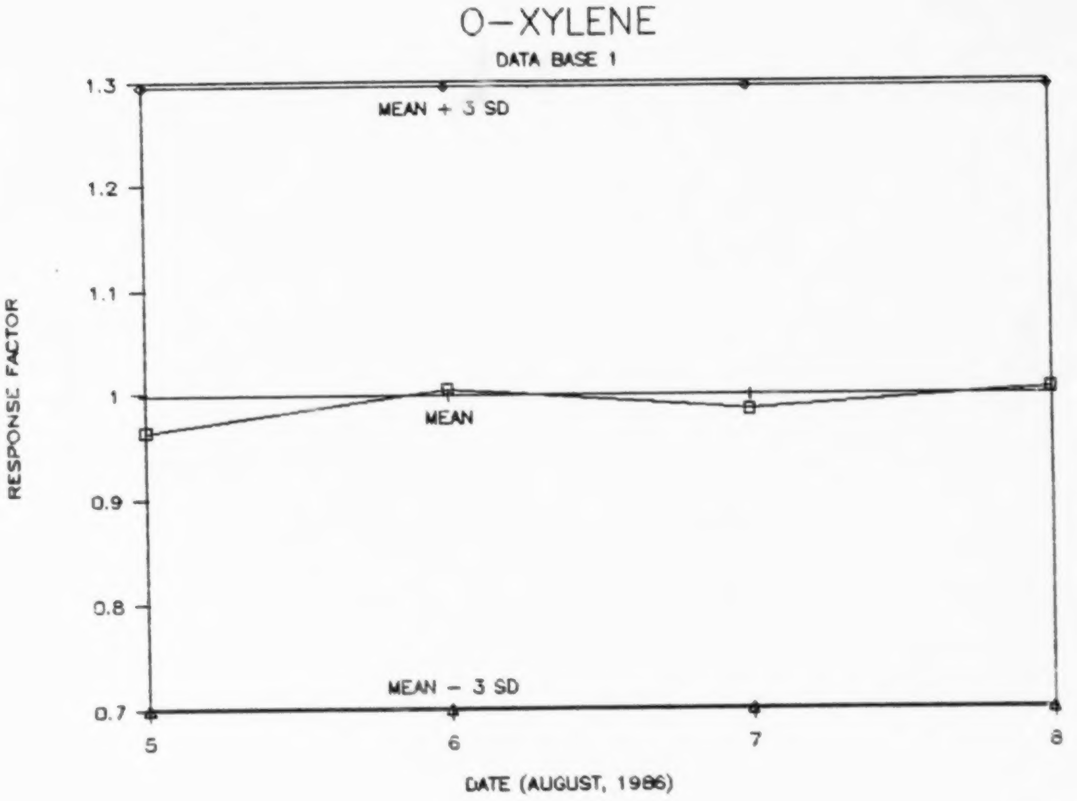

O-XYLENE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN - 3 SD
RESPONSE FACTOR
1.3
1.2
1.1
1
0.9
0.8
0.7
5
6
7
8
DATE (AUGUST, 1986)

Figure E-28

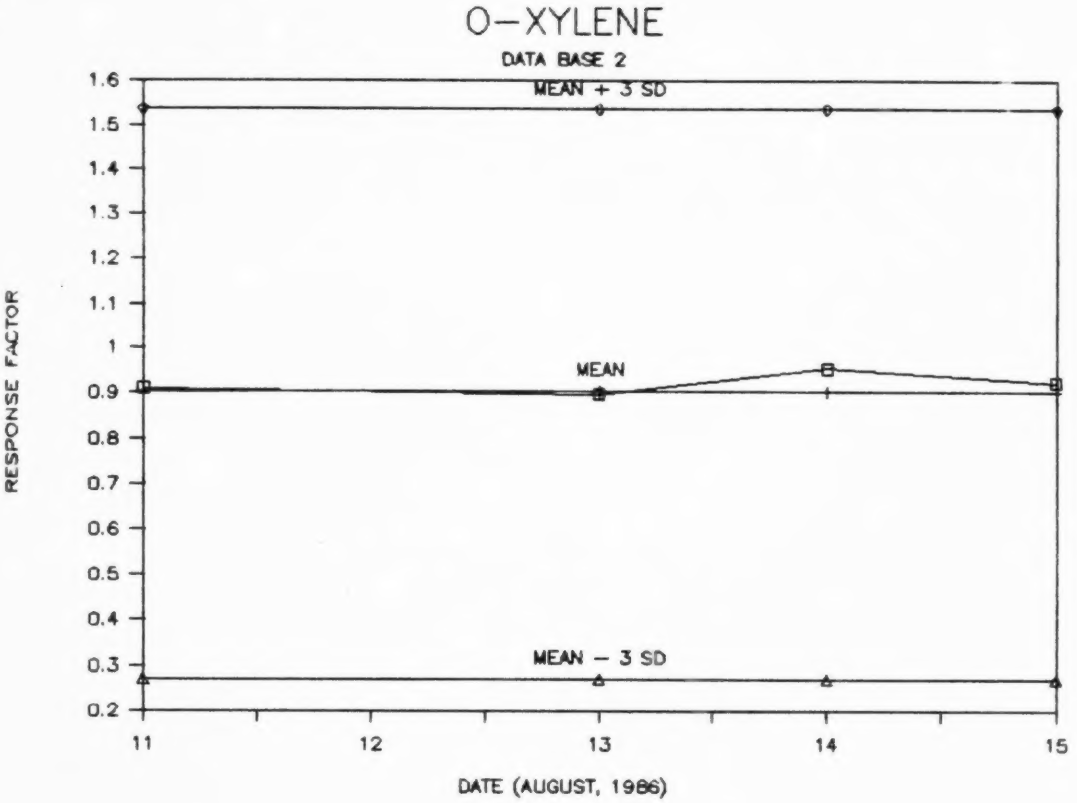

O-XYLENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN − 3 SD
RESPONSE FACTOR
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-29

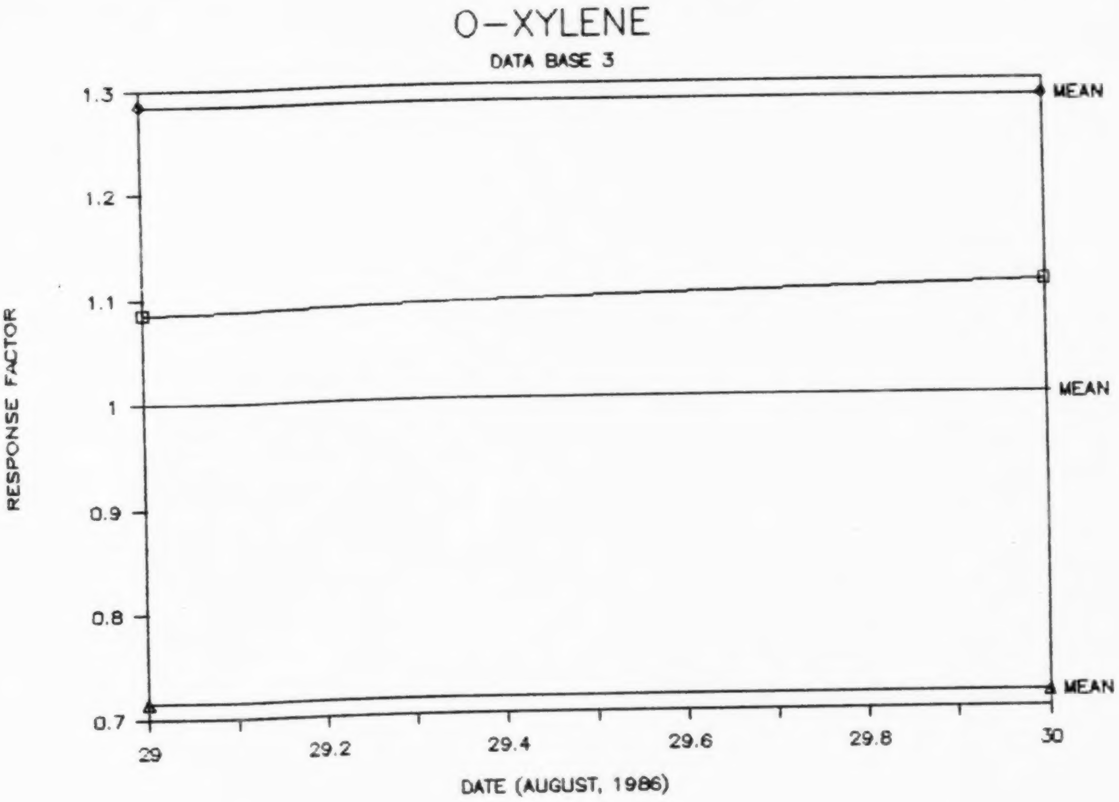
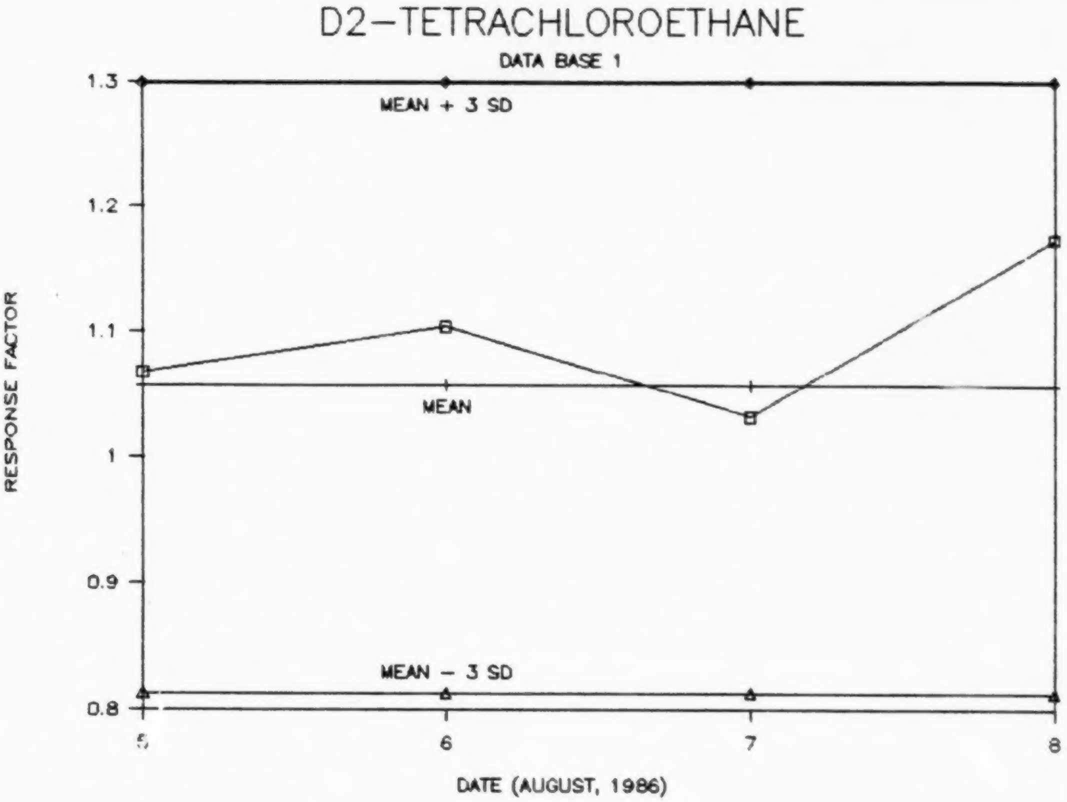

O-XYLENE
DATA BASE 3
1.3
1.2
1.1
1
0.9
0.8
0.7
RESPONSE FACTOR
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-30



D2-TETRACHLOROETHANE
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
1.3
1.2
1.1
1
0.9
0.8
5
6
7
8
DATE (AUGUST, 1986)

Figure E-31

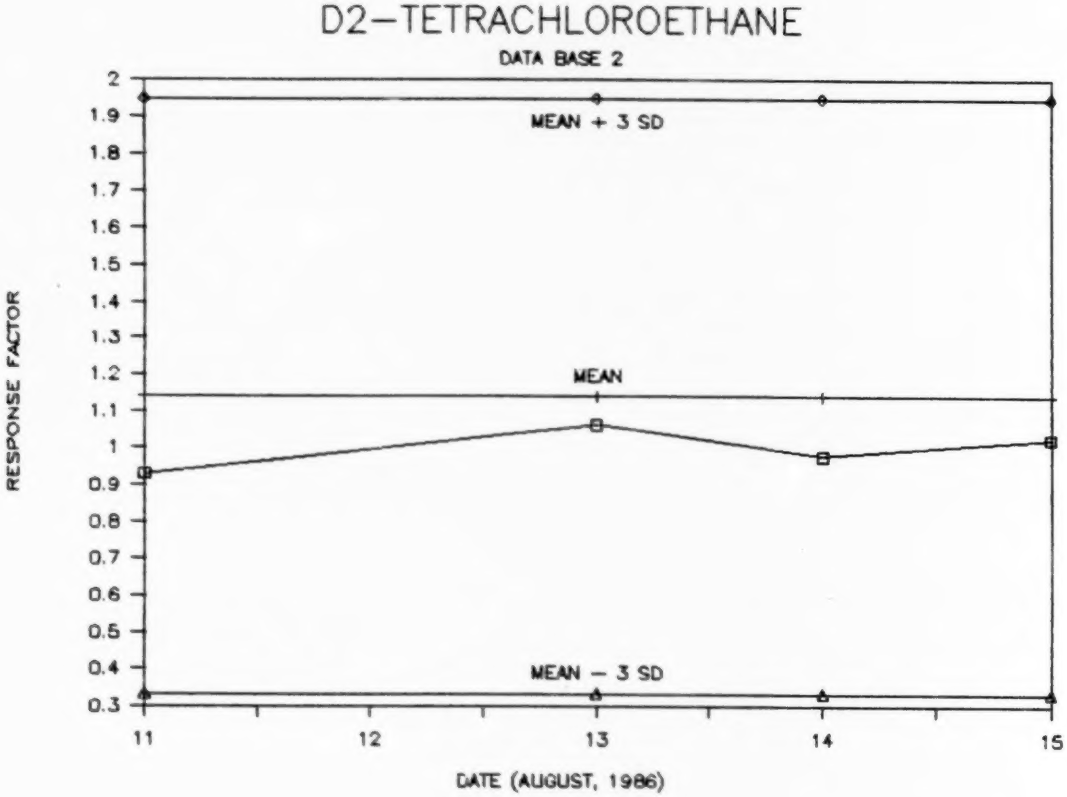
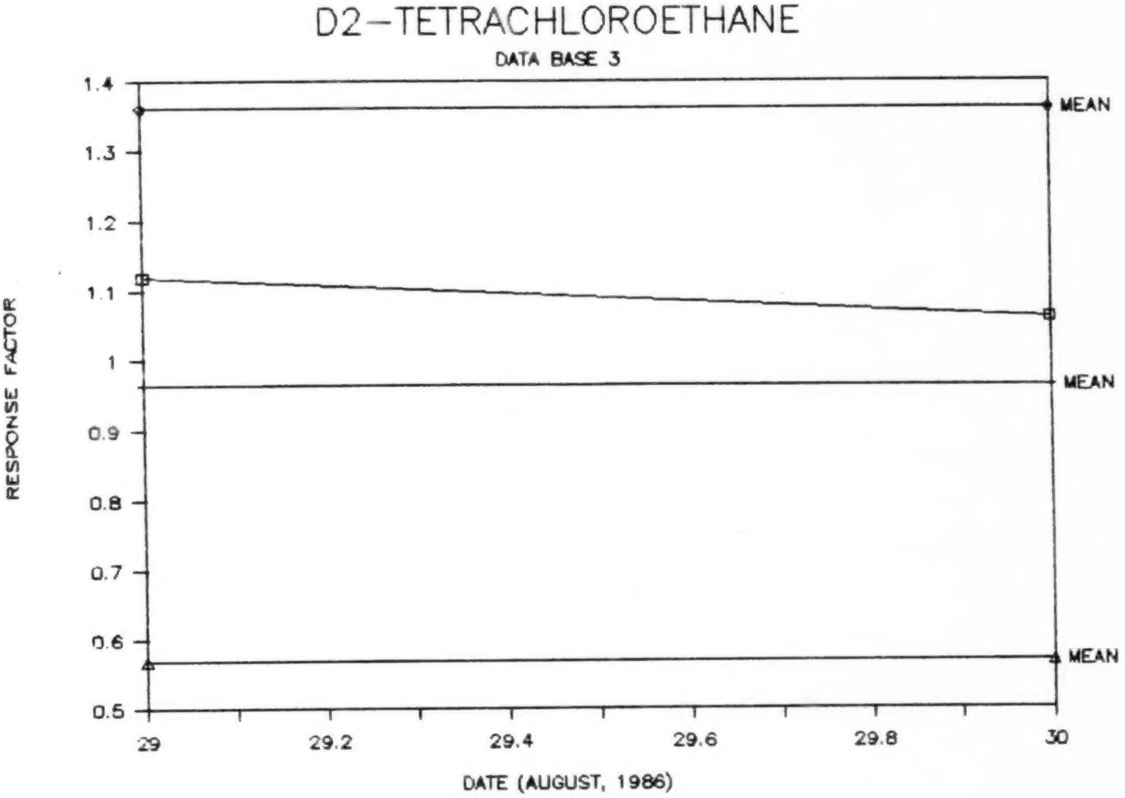

D2–TETRACHLOROETHANE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-32



D2–TETRACHLOROETHANE
DATA BASE 3
RESPONSE FACTOR
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-33

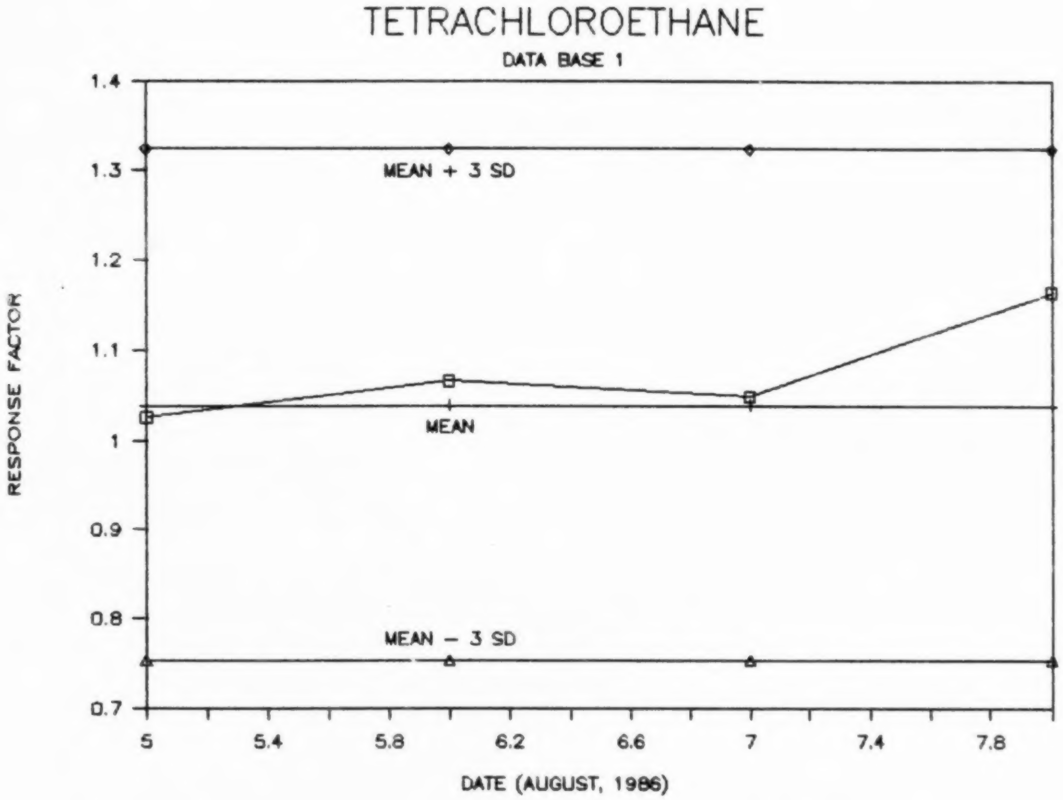

TETRACHLOROETHANE
DATA BASE 1
RESPONSE FACTOR
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
MEAN + 3 SD
MEAN
MEAN − 3 SD
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-34

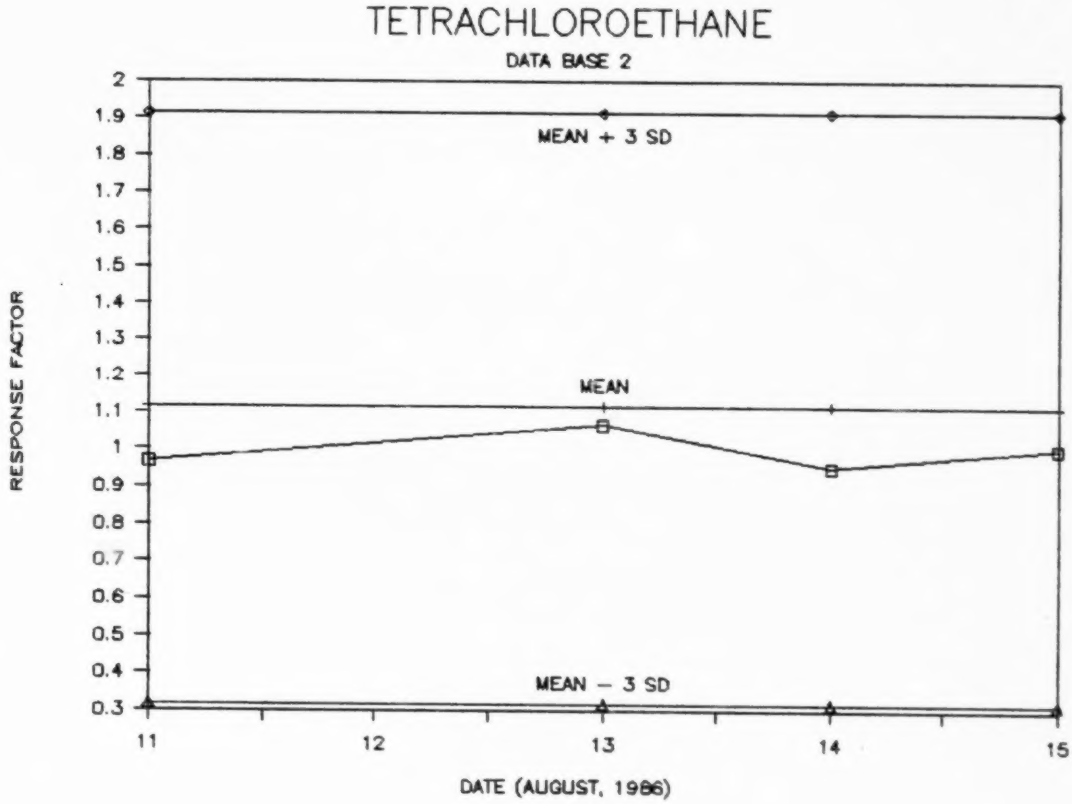

TETRACHLOROETHANE
DATA BASE 2
RESPONSE FACTOR
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
MEAN + 3 SD
MEAN
MEAN − 3 SD
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-35

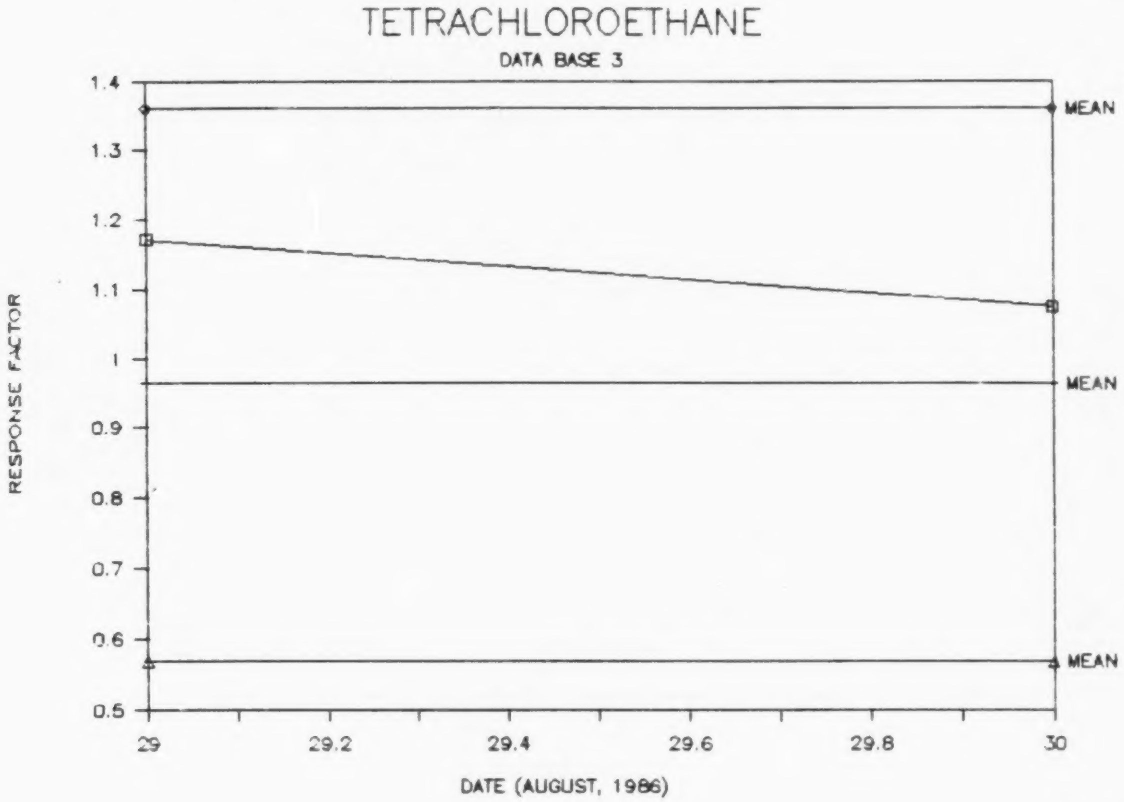

TETRACHLOROETHANE
DATA BASE 3
RESPONSE FACTOR
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-36

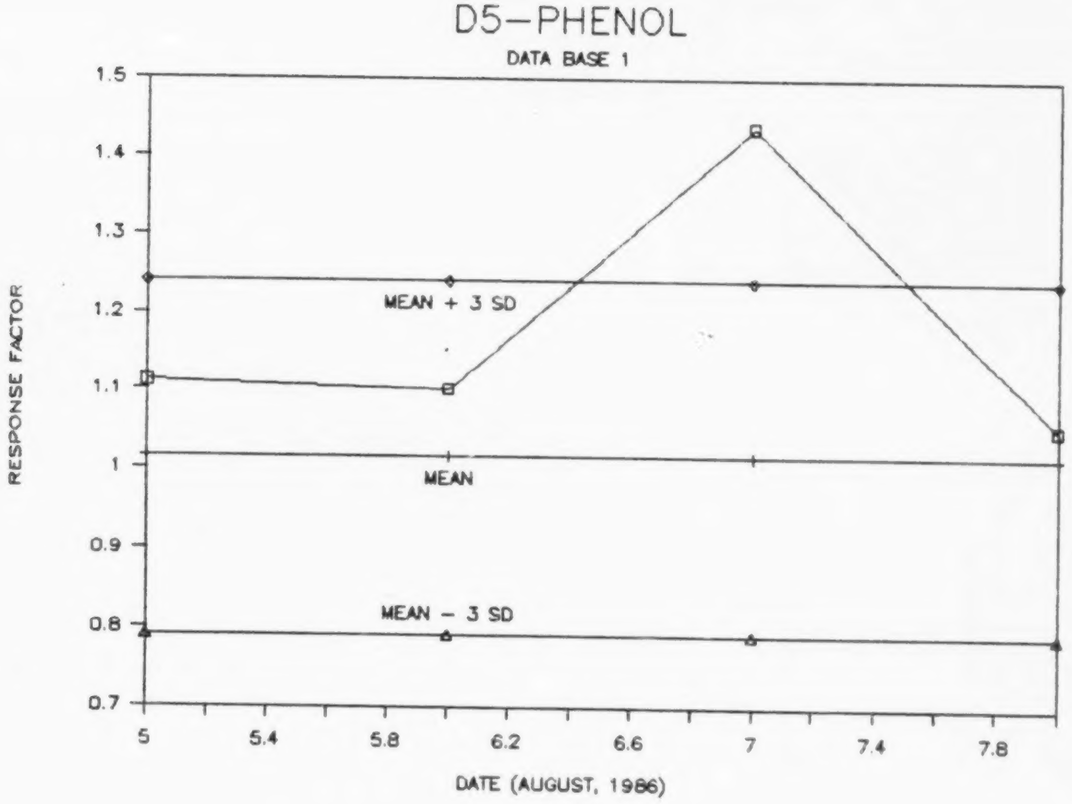

D5—PHENOL
DATA BASE 1
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
RESPONSE FACTOR
MEAN + 3 SD
MEAN
MEAN — 3 SD
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-37

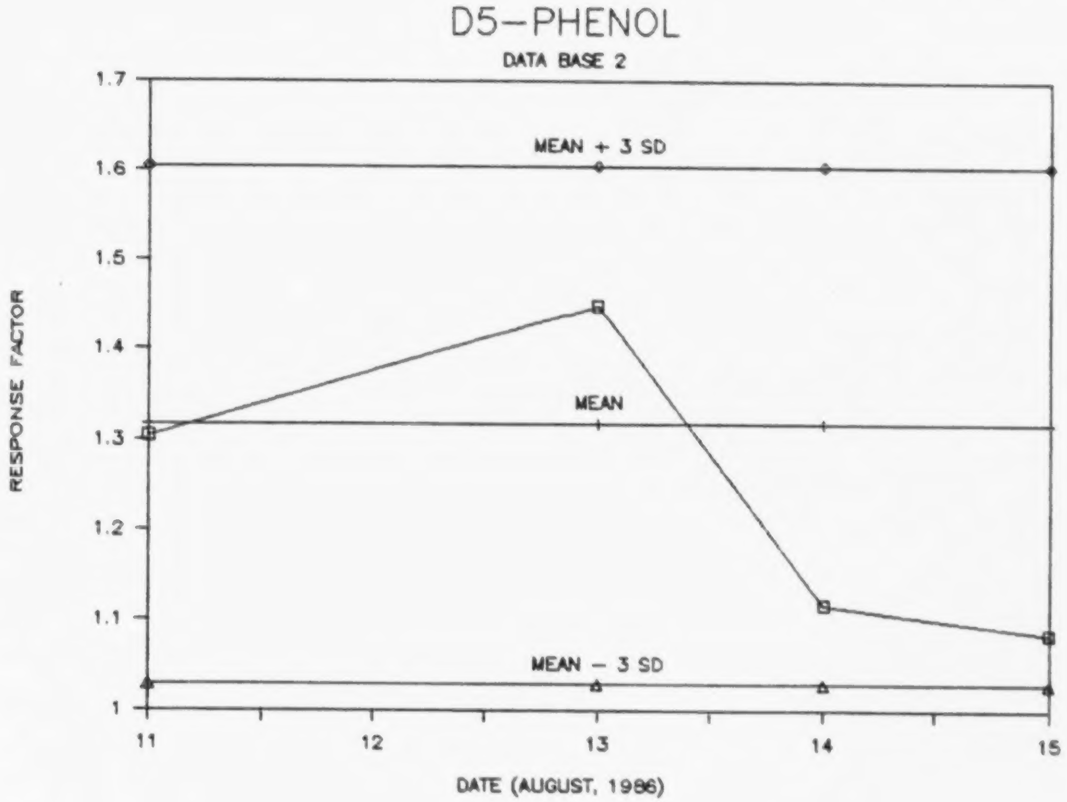

D5-PHENOL
DATA BASE 2
RESPONSE FACTOR
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
MEAN + 3 SD
MEAN
MEAN - 3 SD
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-38

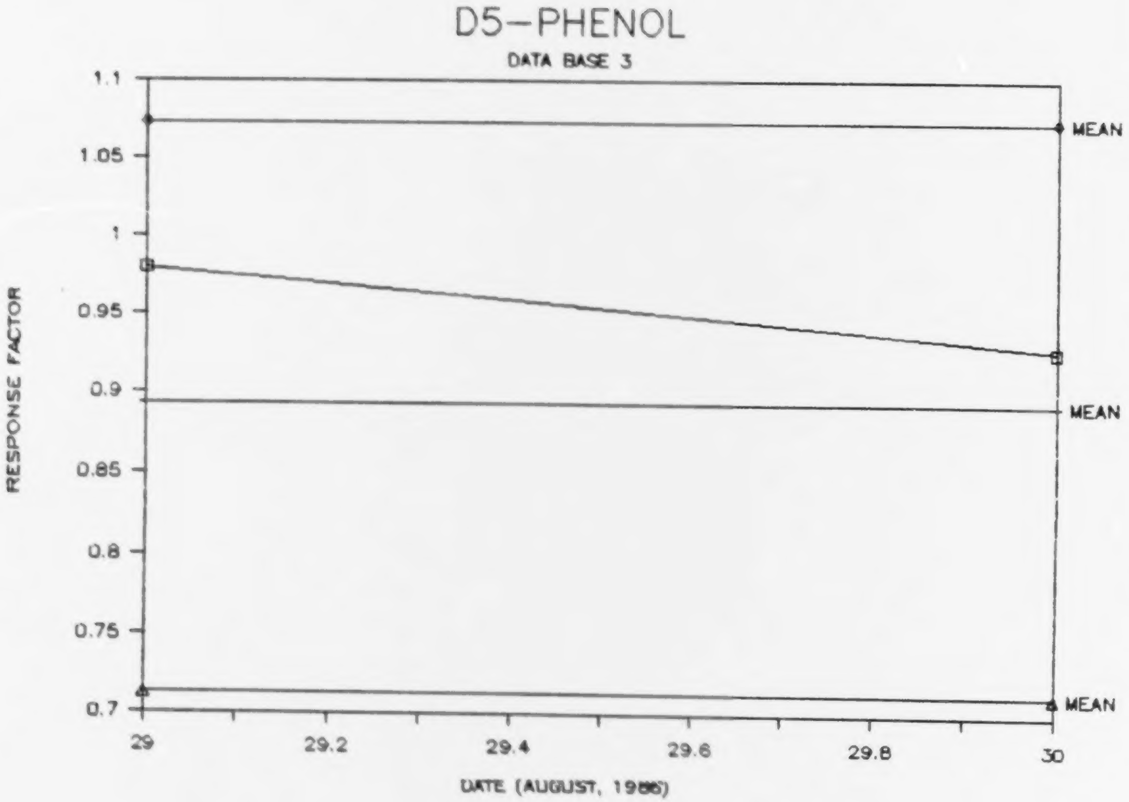

D5–PHENOL
DATA BASE 3
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
RESPONSE FACTOR
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-39

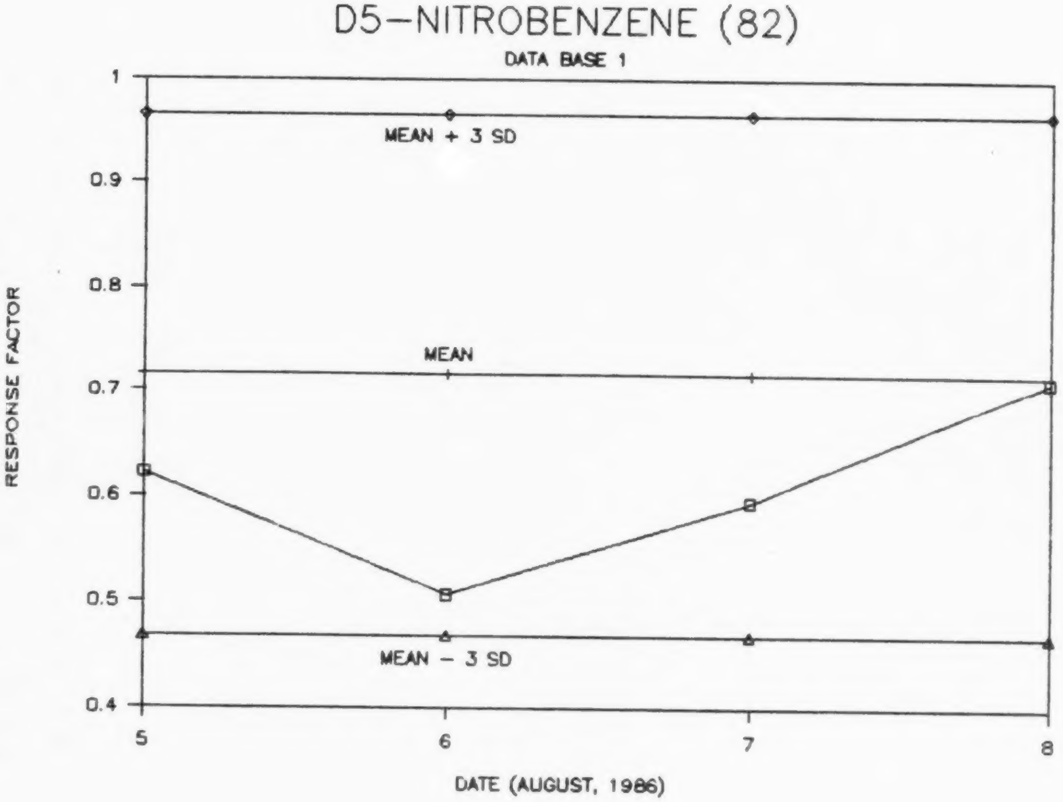

D5–NITROBENZENE (82)
DATA BASE 1
RESPONSE FACTOR
1
0.9
0.8
0.7
0.6
0.5
0.4
MEAN + 3 SD
MEAN
MEAN – 3 SD
5
6
7
8
DATE (AUGUST, 1986)

Figure E-40

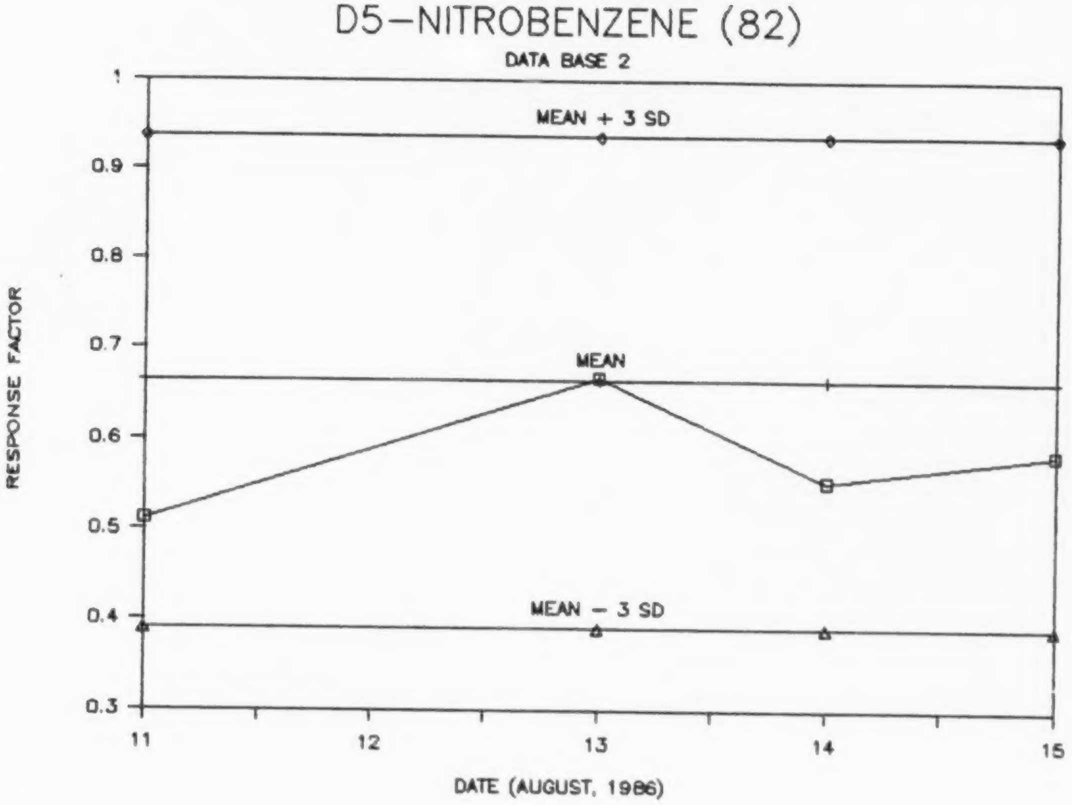

D5–NITROBENZENE (82)
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN – 3 SD
RESPONSE FACTOR
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-41

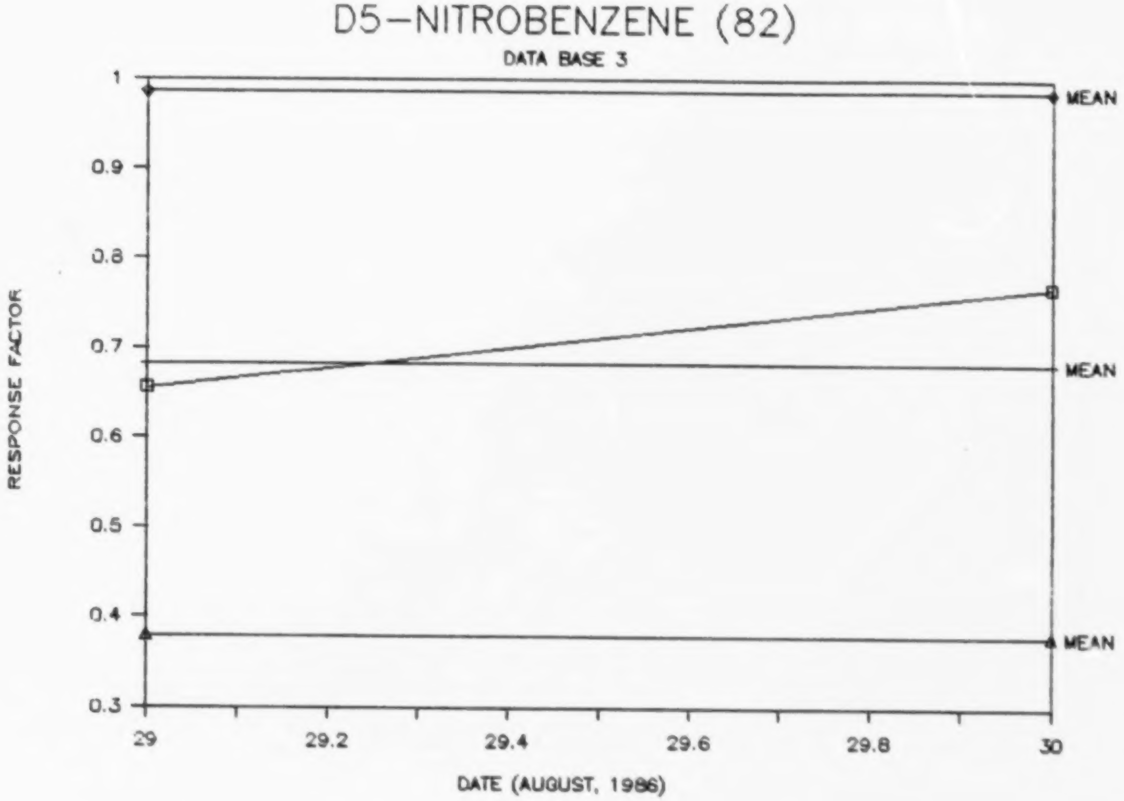

D5–NITROBENZENE (82)
DATA BASE 3
RESPONSE FACTOR
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-42

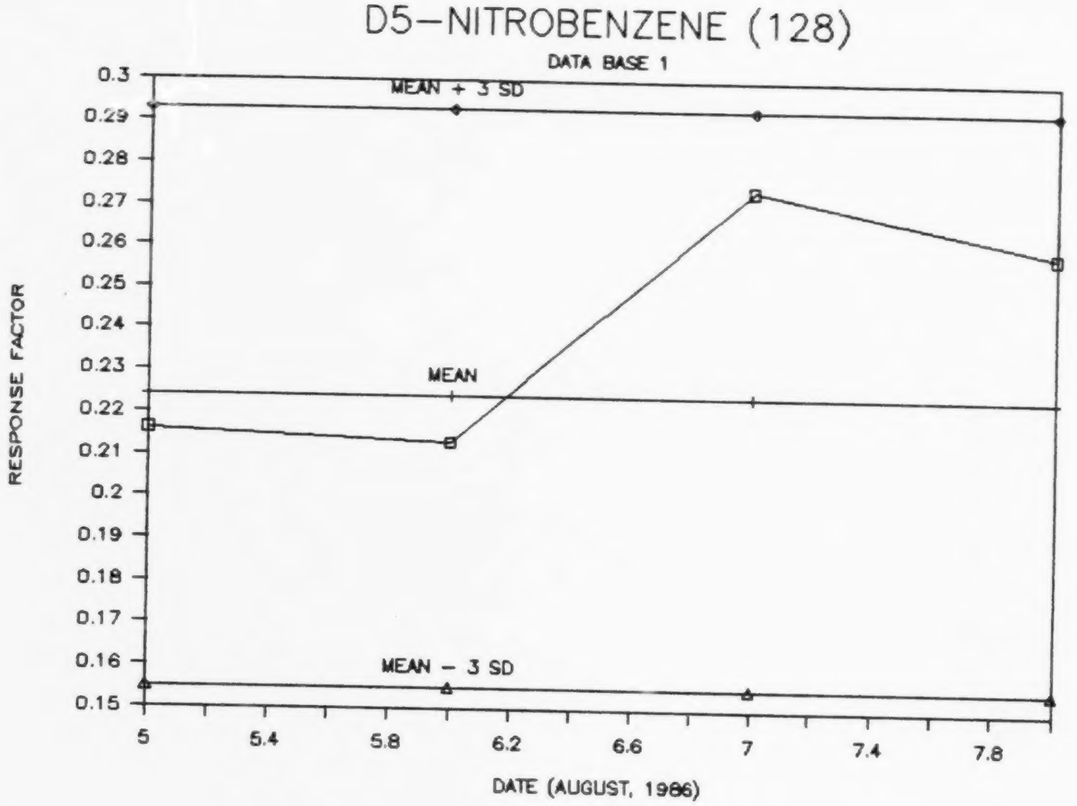

D5—NITROBENZENE (128)
DATA BASE 1
MEAN + 3 SD
MEAN
MEAN − 3 SD
RESPONSE FACTOR
0.3
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
0.19
0.18
0.17
0.16
0.15
5
5.4
5.8
6.2
6.6
7
7.4
7.8
DATE (AUGUST, 1986)

Figure E-43

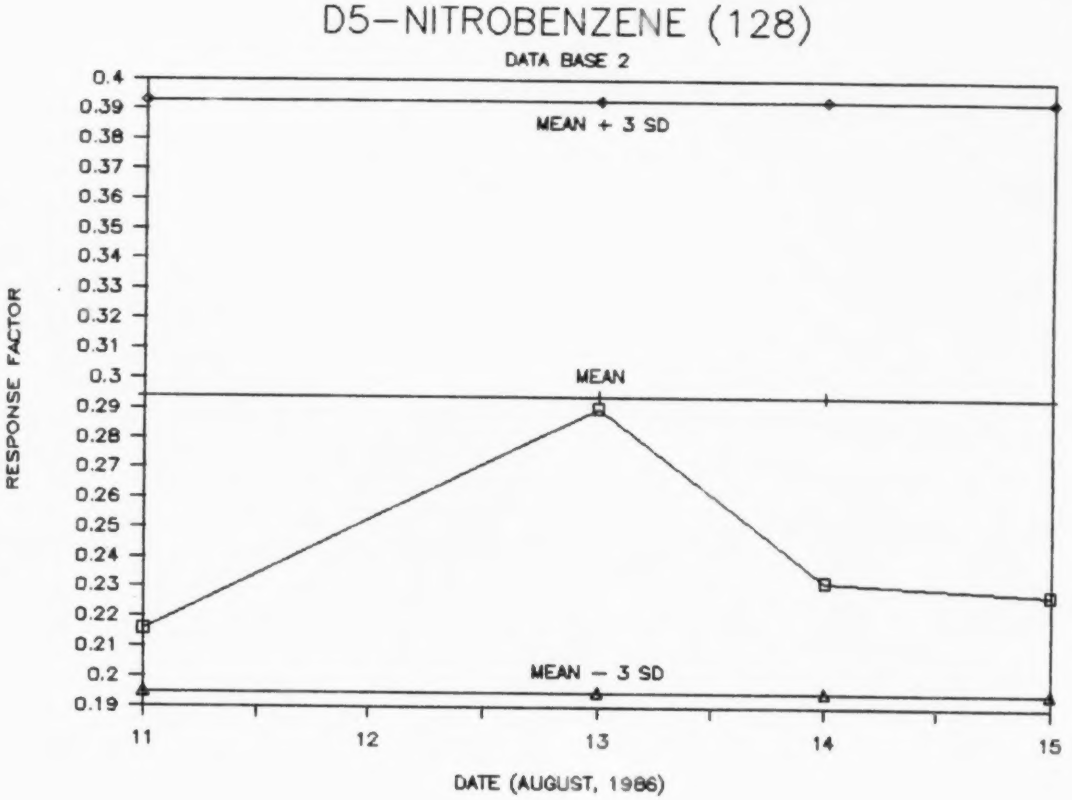

D5—NITROBENZENE (128)
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN — 3 SD
RESPONSE FACTOR
0.4
0.39
0.38
0.37
0.36
0.35
0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
0.19
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-44

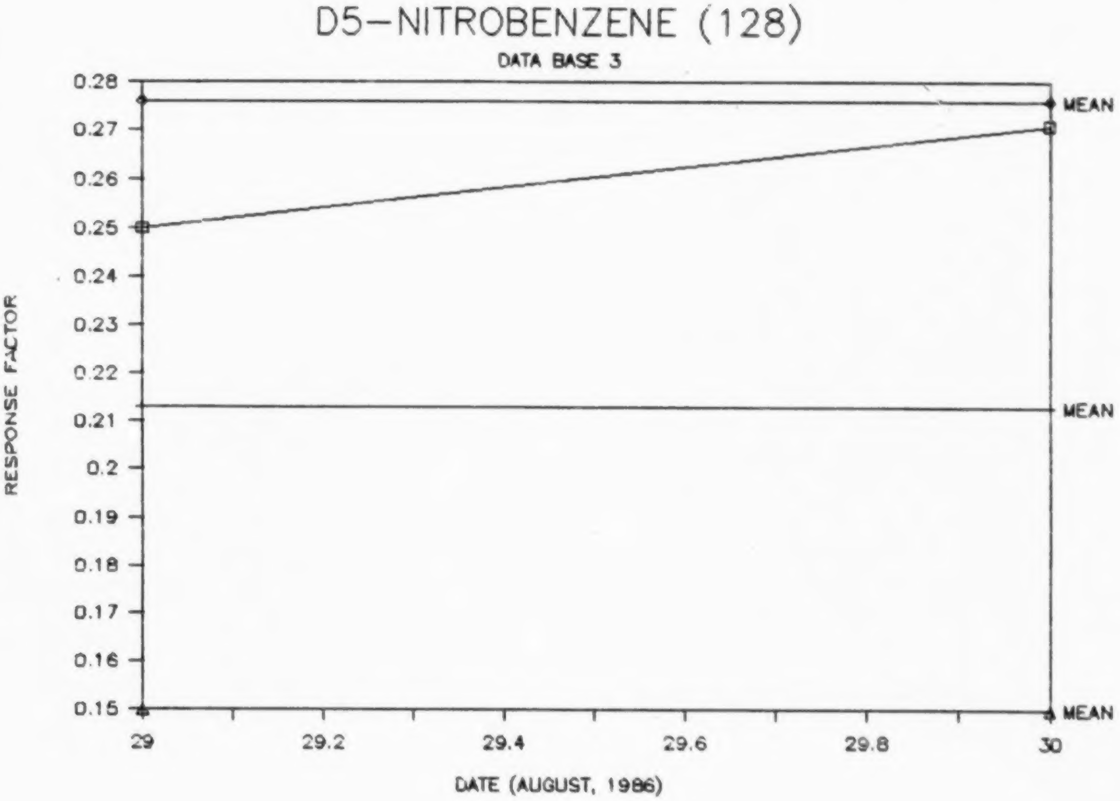

D5–NITROBENZENE (128)
DATA BASE 3
RESPONSE FACTOR
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
0.19
0.18
0.17
0.16
0.15
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-45

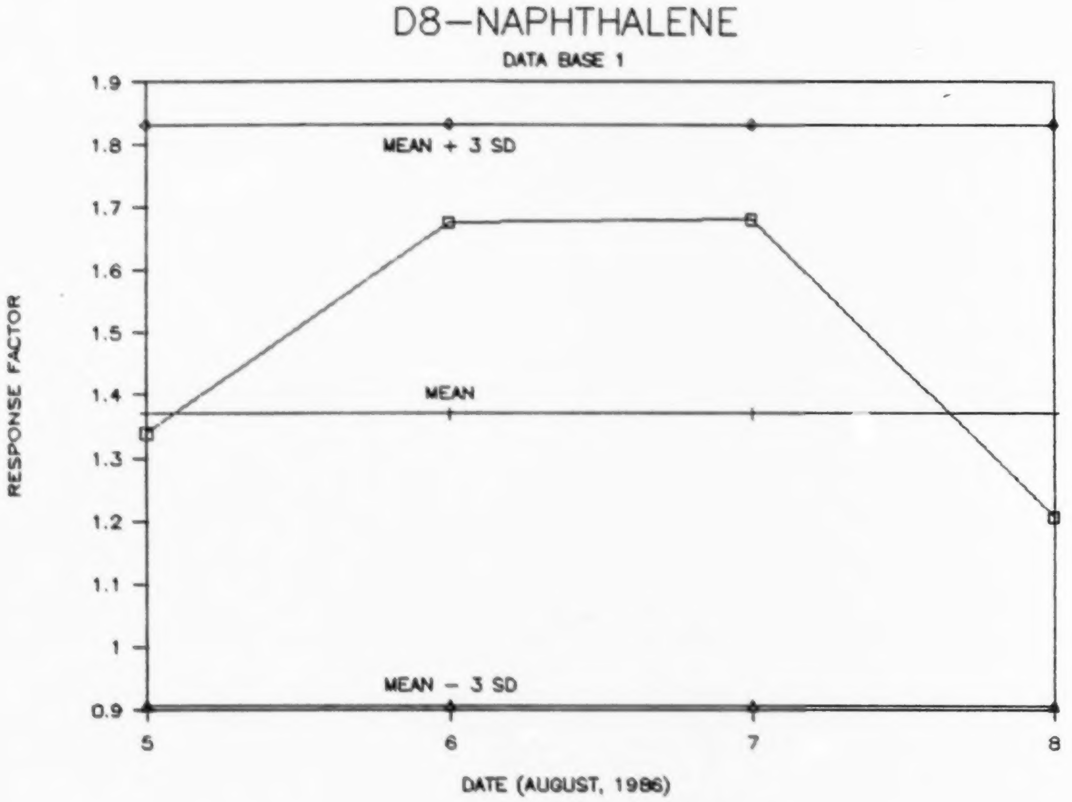

D8—NAPHTHALENE
DATA BASE 1
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
RESPONSE FACTOR
MEAN + 3 SD
MEAN
MEAN − 3 SD
5
6
7
8
DATE (AUGUST, 1986)

Figure E-46

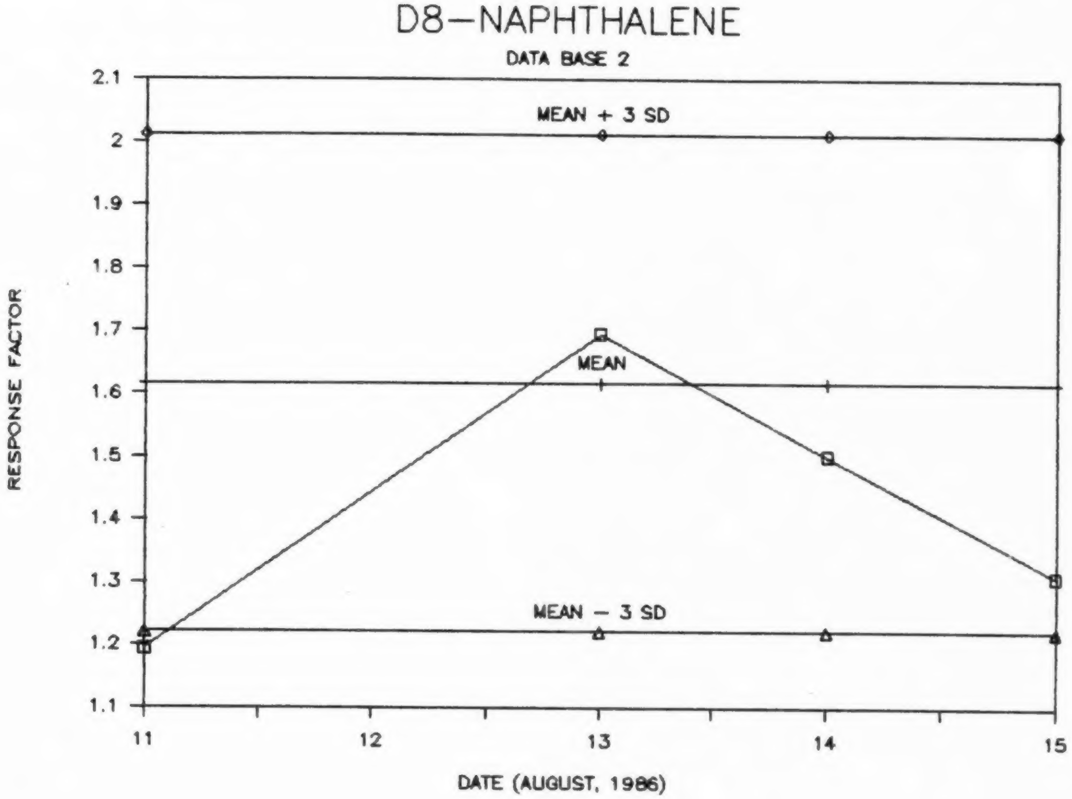

D8—NAPHTHALENE
DATA BASE 2
MEAN + 3 SD
MEAN
MEAN — 3 SD
RESPONSE FACTOR
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
11
12
13
14
15
DATE (AUGUST, 1986)

Figure E-47

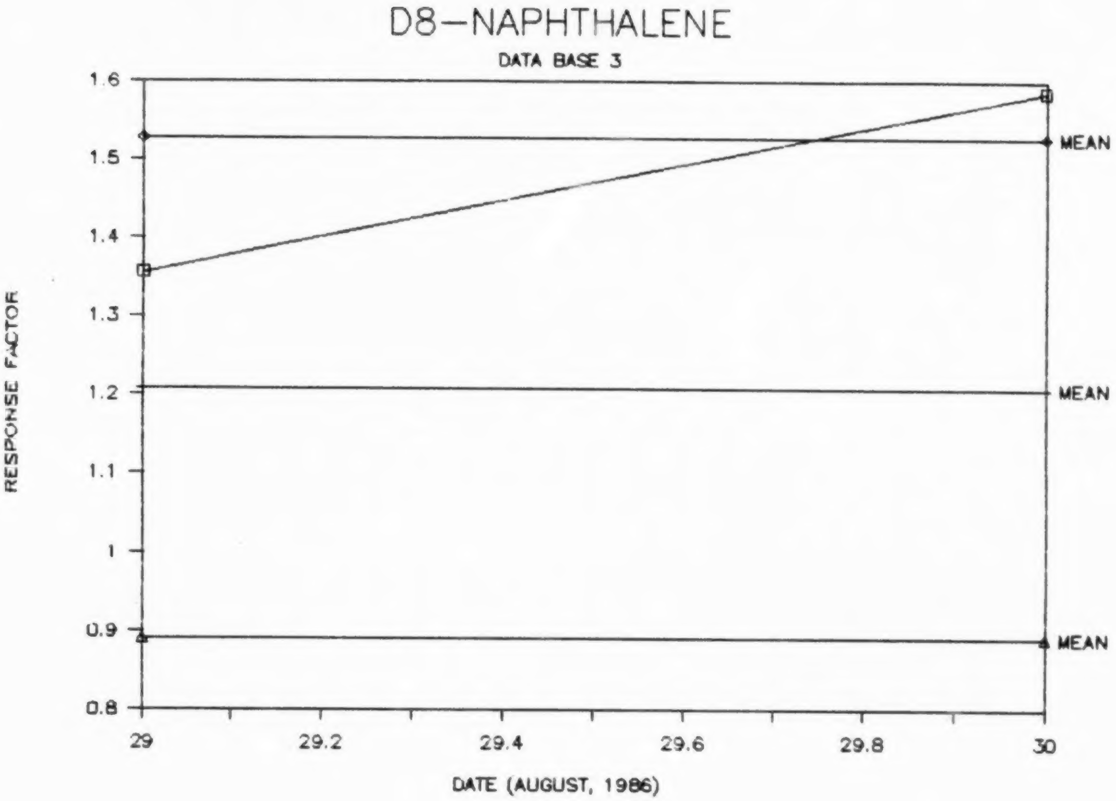

D8–NAPHTHALENE
DATA BASE 3
RESPONSE FACTOR
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
MEAN
MEAN
MEAN
29
29.2
29.4
29.6
29.8
30
DATE (AUGUST, 1986)

Figure E-48

Table E-3. DAILY CALIBRATIONS

		Data Base #1					Date Base #2			Data Base #3	
Compound	M/Z	8/5	8/6	8/7	8/8	8/11	8/13	8/14	8/15	8/29	8/30
d$_5$-pyridine	84	1.309	1.140	1.236	1.669	1.232	1.377	1.181	1.348	1.490	1.655
pyridine	79	1.264	1.114	1.118	1.603	1.190	1.253	1.130	1.303	1.441	1.570
d8-toluene	98	1.299	2.303	2.476	2.604	2.217	2.370	2.250	2.390	2.535	2.635
toluene	92	1.687	1.518	1.642	1.884	1.680	1.574	1.512	1.639	1.786	1.816
tetrachloroethene	164	0.400	0.470	0.516	0.428	0.390	0.532	0.449	0.427	0.418	0.462
d$_5$-chlorobenzene	117	1.598	1.604	1.579	1.705	1.470	1.605	1.567	1.501	1.758	1.799
chlorobenzene	112	1.601	1.666	1.640	1.743	1.466	1.544	1.578	1.546	1.813	1.831
d$_{10}$-ethylbenzene	116	0.945	0.935	1.075	0.908	1.135	1.020	0.975	0.942	0.848	0.885
d$_{10}$-o-xylene	116	0.949	0.990	0.982	0.985	0.893	0.918	0.969	0.931	1.055	1.072
o-xylene	106	0.964	1.004	0.984	1.004	0.910	01896	0.954	0.923	1.086	1.108
d$_2$-tetrachloroethane	84	1.067	1.104	1.031	1.173	0.929	1.062	0.977	1.024	1.120	1.063
tetrachloroethane	83	1.026	1.066	1.049	1.165	0.968	1.065	0.951	1.003	1.172	1.076
d$_5$-phenol	99	1.112	1.101	1.437	1.052	1.304	1.449	1.117	1.085	0.980	0.927
d$_5$-nitrobenzene	82	0.622	0.507	0.595	0.711	0.511	0.667	0.553	0.584	0.655	0.769
d$_5$-nitrobenzene	128	0.216	0.213	0.274	0.259	0.216	0.290	0.232	0.228	0.250	0.271
d$_8$-naphthalene	136	1.339	1.675	1.680	1.207	1.194	1.695	1.500	1.308	1.356	1.586

TABLE E-4. DAILY ANALYSES OF CONTROL SAMPLES

				% of True Value								
Compound	8/5	8/6	8/7	8/13	8/15	8/16	8/29	8/30	8/31	Mean	Standard Deviation	% Coefficient of Variation
d_5-pyridine	117	124	126	147	140	137	114	117	106	125	14	11%
pyridine	117	124	125	160	163	157	115	113	109	131	22	17%
d_8-toluene	123	132	128	139	141	138	100	101	96	122	18	15%
toluene	119	126	119	135	138	136	96	96	92	117	18	16%
tetrachloroethene	98	110	105	91	90	88	105	107	104	100	8	8%
d_5-chlorobenzene	109	117	113	122	122	124	100	99	99	112	10	9%
chlorobenzene	113	122	119	137	135	122	100	98	97	116	15	13%
d_{10}-ethylbenzene	93	95	95	87	85	81	97	94	97	92	6	6%
d_{10}-o-xylene	106	117	112	113	110	124	100	99	102	109	8	8%
o-xylene	114	125	118	138	131	144	100	98	100	119	17	14%
d_2-tetrachloroethane	112	121	117	112	109	112	99	98	100	109	8	8%
tetrachloroethane	115	122	117	126	120	122	99	98	100	113	11	10%
d_5-phenol	87	87	87	71	70	58	94	94	96	83	13	16%
d_5-nitrobenzene	98	92	101	100	94	82	115	114	120	102	12	12%
d_8-naphthalene	102	117	115	104	95	94	113	105	124	108	10	9%

TABLE E-5. RELATIVE ABUNDANCE

M/Z	Ion Abundance Criteria	% Relative Abundance												
		8/4	8/5	8/6	8/7	8/8	8/11	8/12	8/13	8/14	8/16	8/28	8/29	8/30
51	30-60% of mass 198	59.81	55.56	50.63	52.83	50.87	51.53	42.55	50.05	52.49	59.94	34.06	36.19	46.51
68	less than 2% of mass 69	---	---	---	---	---	---	---	---	---	---	---	---	---
69	mass 69 relative abundance	43.41	55.18	50.31	32.56	48.08	38.98	46.68	37.62	44.72	53.01	34.24	44.54	54.76
70	less than 2% of mass 69	---	---	---	---	---	---	---	---	---	---	---	---	---
127	40-60% of mass 198	47.66	54.58	45.78	43.71	51.44	45.06	50.74	42.50	45.51	54.42	46.81	55.69	52.17
197	less than 1% of mass 198	---	---	---	---	---	---	---	---	---	---	---	---	---
198	base peak, 100%	100	100	100	100	100	100	100	100	100	100	100	100	100
199	5-9% of mass 198	7.02	6.87	8.52	6.32	7.40	7.90	7.35	7.80	5.43	7.49	7.47	6.65	6.55
275	10-30% of mass 198	20.04	17.89	19.84	19.43	18.22	22.90	15.43	22.18	22.30	18.05	17.51	16.25	15.17
365	greater than 1% of mass 198	3.05	2.21	3.67	2.83	1.61	6.59	2.55	4.41	4.22	3.23	3.07	1.69	2.25
441	less than mass 443	10.89	7.55	9.92	10.31	4.57	13.86	6.23	10.65	9.44	8.04	10.12	8.22	9.04
442	greater than 40% of mass 198	64.17	46.77	46.41	72.40	50.38	73.75	40.27	75.63	74.15	52.41	56.38	59.51	60.57
443	17-23% of mass 442	13.71	9.22	10.0	14.58	10.43	15.68	6.89	13.06	12.86	10.57	11.43	13.04	11.65